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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 10/075,021
Applicants : James J. Finley and Mehran Arbab
Filed : February 12, 2002
Title : DURABLE SPUTTERED METAL OXIDE COATING
Group Art Unit : 1771
Examiner : Andrew T. Piziali

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. § 1.131

Sir:

I, Mehran Arbab, hereby declare as follows:

1. James J. Finley and I are the named inventors of the invention described and claimed in the above-captioned application. I assigned all my rights, titles and interests in the above captioned application to PPG Industries, Inc. (hereinafter also referred to as "PPG"). Mr. Donald Lepiane, a retired employee of PPG and now a consultant to PPG, has informed me that the present assignee of the above-captioned application is PPG Industries Ohio, Inc, a wholly owned subsidiary of PPG.

2. In May of 1989 I began my employment with PPG, and during my employment with PPG, I have worked at its Glass Technology Center located in Harmarville, Pennsylvania, having various assignments relating to sputter coating substrates, e.g. glass and plastic substrates; glass compositions and processes for making flat glass, and technical administration. At the present time my title is "Associate Director" having responsibility for research, development and technology transfer of flat glass products and processes.

3. On August 6, 1993, I signed a Memorandum of Invention entitled "HARDENED METAL COATINGS BY MSVD PROCESSING" having attachments thereto (hereinafter also referred to as "MOI") describing a concept conceived by James J. Finley and myself to sputter a metal in an atmosphere having reactive and non-reactive gases. The MOI was forwarded to the Patent Department of PPG. The Memorandum of Invention form was one way I used to submit concepts I conceived relating to my work at PPG to the Patent Department of PPG to have the concepts considered for patent filings.

4. Attached Exhibit A is a copy of the MOI that I signed on August 6, 1993, and was forwarded to the Patent Department of PPG. The attached copy of the MOI is redacted to omit dates prior to February 4, 1993, and/or PPG confidential information. Shortly after the MOI was forwarded to the Patent Department of PPG, I received an interoffice correspondence signed by Ms. Donna Seidel Assistant Patent Counsel for PPG advising me that the MOI was received and that Patent Department No. 93-51 was assigned to the disclosure. A copy of the interoffice correspondence I received is attached hereto as Exhibit B. Shortly after receiving the interoffice correspondence, I was advised that a patent application covering the concept disclosed in the MOI was filed.

5. I signed the MOI on August 6, 1993; however, the conception of the idea described under Section C Description of Invention of the MOI was had before February 5, 1993. More particularly, Section G of the MOI has the signature of Mr. Dennis Postupack a former employee of PPG acknowledging that the invention was disclosed to him on September 11 of a year prior to February 5, 1993.

6. On February 4 and 5, 1993, I visited PPG's Works 28-8 in Evansville, Indiana to supervise the deposition of titanium metal films on glass substrates by sputtering a titanium cathode in an atmosphere of oxygen and argon. The information obtained in the laboratory was used to prepare the sputter coating apparatus. The attached copies of my notebook pages dated February 4 and 5, 1993, summarizes relevant process parameters used to make full size 4 mm thick automotive glass transparencies practicing the invention, e.g. DC current applied to the titanium metal cathode (target), number of cathodes and line speed, are summarized on the pages for February 4, 1993, and relevant coating parameters, e.g. color coordinates including the data under the columns "x", "y", "Y", are summarized on the pages for February 5, 1993. More particularly, prior to coating the automotive glass

transparencies, setup glass samples were coated with a titanium metal film by sputtering a titanium cathode in an atmosphere of oxygen and argon. The setup samples were coated to bracket the range of DC current to the cathode and select a line speed to move the full size automotive glass transparencies under the cathodes. The coated setup glass samples were then heated at about 600°C in air to oxidize the titanium metal film coated on the setup samples. The oxidation of the titanium film deposited on the setup samples is not detailed in my notes; however, the color coordinates "x", "y", "Y" on the page dated February 5, demonstrate that the titanium film was oxidized. This information collected on February 4 and 5, 1993 was used to choose the coater settings to sputter coat a desired thickness of a titanium metal film on full size 4 millimeter thick automotive glass transparencies by sputtering a titanium metal cathode in an atmosphere of oxygen and argon on February 5, 1993. The automotive glass transparencies were heated at a later time in a tempering furnace at a PPG facility.

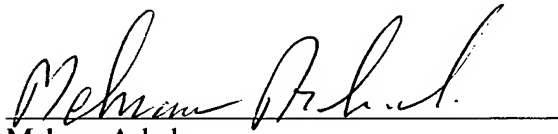
8. The copies of the ATD Monthly Letters of Exhibit A were authored by me and relate to the invention disclosed in the MOI, and in the above-captioned application. The report for December 21 of a year prior to February 5, 1993, does not have a heading and a date. My recollection is that the heading and date are on the previous page, which was not copied; however based on my recollection the first report has a date of December 21 of a year prior to the February 5, 1993. The second ATD Monthly Letter is dated February 22, 1993, and summarized the work conducted by me on February 4 and 5, 1993, at PPG's Works 28-8 and discussed above in Paragraph 7 of this Declaration. The ADT Monthly Letters for March 25, April 26, and May 21, 1993, report on additional activity regarding the concept of depositing a titanium metal film on a substrate, e.g. a glass substrate, by sputtering a titanium metal cathode in an atmosphere of oxygen and argon.

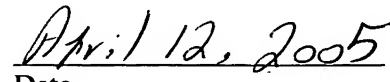
9. To the best of my recollection work continued after April 1993, on the concept of sputtering a metal in an atmosphere of oxygen and argon, and additional ADT Monthly Letters were written. To the best of my knowledge, in accordance to PPG's Retention Policy, ATD Monthly Letters authored by me after May 21, 1993, and copies thereof have been destroyed.

10. The ATD Monthly Letters and the Memorandum of Invention form of Exhibit A are a record of my activity to demonstrate the required evidence of conception and

diligence from a date before February 5, 1993, until the filing of a patent application covering the embodiments of the invention disclose in Exhibit A.

11. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.


Mehran Arbab


Date

P MEMORANDUM OF INVENTION

Entry No. TG-93-51

To Patent Department -

AUG 18 1993

From (Location) Harmarville

Disclosed herein for consideration is a record of invention as described below:

A. BRIEF TITLE OF INVENTION

Hardened metal coatings by MSVD processing

B. PURPOSE OF INVENTION

Metal coating is hardened during sputtering for subsequent use in shipping or processing, e. g., cold end, heat strengthening, bending and tempering.

C. DESCRIPTION OF INVENTION

Oxygen gas is bled into a vacuum system along with argon gas during the sputtering of a metal. The quantity of oxygen gas is kept at levels less than that required to switch from metal to oxide sputtering mode. The coating sputtered in this range of mixed argon/oxygen gas is only slightly higher in transmission than a coating sputtered only in argon, and the sputtering rate is approximately that of the metal. The amorphous metal coating produced using this method is significantly harder than the crystalline metal coating produced by sputtering in pure argon gas. Higher oxygen/argon gas ratios produce a harder coatings. This coating could be heated to produce a haze free, dense, crystalline metal oxide coating with first surface durability. This is an extremely cost effective way to produce thick metal oxide coatings with applications as interference color coatings with selected chromas. Oxygen is the preferred gas; nitrogen has the same effect, however, the heated coating is extremely hazy. The preferred metals are titanium and zirconium. Other metals include Al, Hf, Nb and V.

Attach supplemental sheets as necessary.

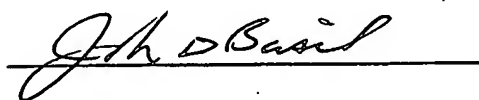
D. LIST PERTINENT PATENTS OR PUBLICATIONS KNOWN TO YOU

A. Inove, H. Vamagata & T. Masumoto; Nitrogen-Induced Amorphization in Al80Ti20 Films Prepared by Reactive Sputtering; Materials Letters 16 (1993), pages 181-184

NOTE: IN SECTIONS E, G, AND L, PLEASE TYPE OR PRINT NAMES ADJACENT ALL SIGNATURES.

E. WITNESS TO FOREGOING DESCRIPTION AND TO THE SIGNATURE(S)
OF INVENTOR(S)

SIGNATURE OF INVENTOR(S)

8/6/93
DATEAugust 6, 1993
DATEJohn D. Basil
TYPE OR PRINTJames J. Finley
TYPE OR PRINT_____
DATEAugust 6, 1993
DATE_____
TYPE OR PRINTMehran Arbab
TYPE OR PRINT

IMPORTANT: If there is any record of the invention preceding the date of this memo, please fill in the appropriate data on the reverse hereof.

F. WHEN DID THE INVENTION FIRST OCCUR TO YOU (GIVE DATE)

Sept 11,

G. WHEN AND TO WHOM, OTHER THAN THE CO-INVENTORS, DID YOU FIRST COMMUNICATE THE INVENTION (GIVE DATE)

D.S. Postupack, Sept 11,

I (WE) ACKNOWLEDGE THAT THE INVENTION WAS COMMUNICATED TO ME (US) ON THE DATE INDICATED ABOVE.

SIGNED

Dennis Postupack

TYPE OR PRINT

DENNIS. POSTUPACK

SIGNED

TYPE OR PRINT

H. WHEN AND WHERE WAS THE FIRST SKETCH, DRAWING, OR PHOTOGRAPH, IF ANY, MADE OF THE INVENTION. IDENTIFY AND ATTACH COPY.

I. WHEN WAS THE INVENTION FIRST DESCRIBED IN WRITING. GIVE DATE AND IDENTIFY NOTEBOOK, REPORT OR OTHER SOURCE. ATTACH COPY.

Sept 11, Data Book No. 6296 pages

J. IDENTIFY PERTINENT DESCRIPTIONS, REPORTS, SUMMARIES, DRAWINGS, PHOTOGRAPHS, ETC. SUBSEQUENT TO I ABOVE.

VET036 sample series deposition parameters, Wks 28 Line 8, February 5, 1993

Test results for Taber abrasion analysis of the above samples, March 22, 1993

Plant trial notes, Mehran Arbab, February 4 & 5, 1993

K. WHEN (GIVE DATE) AND WHERE WAS THE INVENTION EITHER FIRST MADE (MACHINE OR PRODUCT), OR FIRST PERFORMED (PROCESS).

Sept 11,

L. WHEN AND BY WHOM WAS THE INVENTION FIRST TESTED ANYWHERE FOR PERFORMANCE (GIVE DATE, AND NAMES OF OBSERVERS)

Sept 11, P.S. Postupack

I (WE) ACKNOWLEDGE THAT I (WE) OBSERVED THE PERFORMANCE TEST ON THE DATE INDICATED ABOVE.

SIGNED

TYPE OR PRINT

SIGNED

TYPE OR PRINT

M. HAS THE INVENTION BEEN PUBLISHED OR COMMUNICATED OUTSIDE THE COMPANY (GIVE DETAILS)

no

N. IF A PRODUCT RESULTING FROM THE INVENTION HAS BEEN USED OR SOLD ANYWHERE, STATE WHEN AND WHERE

End of year - windshields and sidelights (not oxidized) were sent to GM; - Samples
of oxidized coatings were shown to GM, Chrysler, Toyota

TITLE

DATE

Tues, Sept 11

Sputter Ti films under different conditions of cathode scanning speed and current. oxygen flow

Ti-12 Current-15; scan-max Rate 35 7 passes to 10.5%
abrasion resistance is VG

Ti-13 Current-15 scan-max⁶ Rate 35 4 passes to 8.8%
abrasion resistance is POOR

Ti-14 Current-10; scan-max Rate 30 11 passes to 10.1%
abrasion res VG

I took pictures of Ag splot on Au (see time since splot is

Wed, Sept 12

Sputter Ti films also at 15 amps and scan of 6 with different amounts of O₂

Ti-15 Rate 36; O₂ flow 9 Ar flow 18; 8 passes at "6" and 1 pass at "8" to 9.4% T. abrasion res Excellent. reflectance is brownish

Ti-16 Rate 36; O₂ flow 4.5 Ar flow 18.4; 5 passes at "6" to 9.2% T. abrasion res - Excellent; reflectance is slight brownish, between metallic and Ti-15 ref.

Ti-17 Rate 36; O₂ flow 1.5; 5 passes 9.0% T abrasion excellent

Thurs, Sept 13

Sputter Ti in N₂

Ti-18 (Sputtered 9-12) Pure Argon (NO O₂ or N₂)
abrasion resistance POOR

EXPERIMENT CONDUCTED BY

James J. Grah

WITNESSED BY

DATE

Sept 13

TITLE _____

DATE _____

Ti-19 Rate (17-18); N_2 flow 10.5 (Scrape A-ball 53)
 12 passes to 22.4% T; Abrasion Res - Ajax excellent
 Primie-poor; Bronze ref.

Ti-20 Rate 33; N_2 flow 5* (+ half ball); 8 passes,
 10% T; Excellent abrasion resistance for
 both Ajax and Primie.; Goldish Reflector
 $R = 46 \text{ @ } 15\%$

Ti-21 Rate 35; N_2 flow 1.5; 5 passes to 8.5% T;
 Abrasion - Ajax VVG, Primie VVG. $R = 85 \text{ @ } 15\%$

Ti-22 Rate 27-28; N_2 flow 3.5, O_2 flow 2.5; 14 passes
 10.7% T

Fri, Sept 14

Try glass cleaned in washer (covered)

Ti-23 Rate 35; O_2 flow - 1.5; 5 passes to 8.7% T
 Abrasion res VG

~~REDOX~~ Try glass CeO₂ polished but no cover

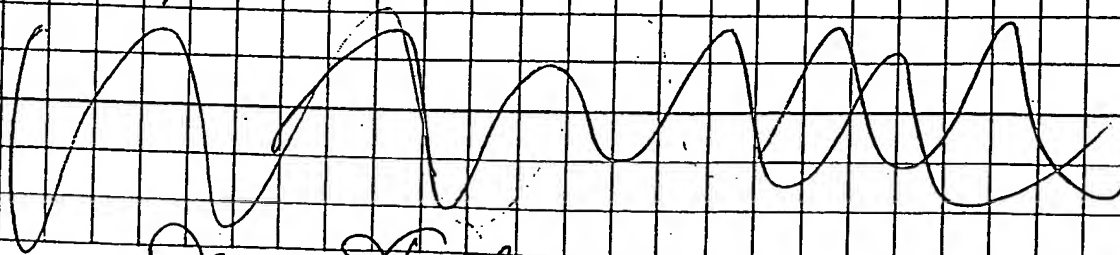
Ti-24 Rate 35; O_2 flow - 1.5; 5 passes, 7.7% T
 Abrasion res VG

Look at #1503 (3rd/En 70 - $As_2 - (Zr/Sr)_2O$ film
 under opt. lens. Show no spots, defects etc.

Mon Sept 17 to Wed Sept 27

Wardshields for GMI coated with Ti

I will give details after project
 is completed



EXPERIMENT CONDUCTED BY

James J. Smith
 DATE Sept 24, 1967

WITNESSED BY _____

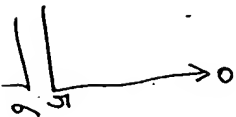
DATE _____

Also try the Zn Sn!

VE036

35
38
41
44

VE036



4:1 PM 1:14

5:18 PM

2-5-93

*

Sample no	Amx (g?)	Qx	S	Y
VE 2	38 (no)	0.022		
6	43	0.2227	0.1745	10.42
7	39	0.3139	0.2359	11.70
8	37	0.3795	0.3310	11.11
9	38	0.3545	0.2924	14.2
10	40	0.2912	0.2151	10.39
11	41	0.3655 0.2225	0.1884	10.15
12 (48 9, 4m)	38			
13	40.5			

Creighton windshields: 12

6: AT 42.4

8: AT 40.5

4mm Sile 1:14

27 88 AT 40.5 (3) stuck 33/30x 41 sample 1/20
 9 88 AT 48.5 (20x 20) stuck 67/30x 2' sample 1
 9 AT 44 blue stuck 47/30x 2' sample 1
 9 AT 39 (7) stuck 57/20x 2' sample 1

Run IL5 for 13

* 520-1 Cherry Blazer F.D.
Line 4

More than fifty 4mm side-lites (clear, 520-1 pattern) were coated with 4 Ti thicknesses targeting 4 different color coordinates. These samples were subsequently tempered on line 28-4 (W. Zimmerman). Presumably as a result of the undefined heat pattern (too few samples were available), all of the lites developed varying degrees of near-edge crazing. This issue, as well as the unknown effects of cold end processing of the coated substrate (i.e., cutting, edging, and washing) remain to be resolved.

ATD Monthly Letter

Date: 12/21/

Program Category:

Department:

Title/Project No.:

Author: MA

ATD Monthly Letter

Date: 2/22/93

Program Category:

Title/Project No.:

Department:

Authors:MA

Project Team:

Program Category:

Title/Project No.:

Department: Vacuum-Auto

Author:MA

Project Team:

* Technical Highlights: A one day trial at wks 28-8 was dedicated to a preliminary evaluation of fabrication of the monolithic, high transmission, colored coatings. This trial was based on the Pastel concept developed at the lab. (JJ Finley), where an opaque metallic Ti (or other metals or alloys) deposited on glass, is oxidized during the tempering (or bending) process. Depending on its thickness, the resulting oxide layer imparts a variety of reflective colors to the glazing. The reason for the deposition of the initial coating in the metallic mode is to exploit its high deposition rate (as compared to the reactive sputtering of, e.g., TiO_2) and to make the Pastel concept cost effective and compatible with the existing coater capabilities. The concern with this approach is, however, the mechanical durability of the metallic titanium coating.

With the help of an xy color chart generated from the laboratory samples, a specific target color (ca. $x=0.2782$, $y=0.2028$) was obtained in a short period of time. However, during this trial, we concentrated only on samples cut from the center of the coated lites; that is, the potentially significant gradient problems were not examined.

The concern about mechanical durability of the metallic coating was addressed using the partial oxidation concept similar to that used in the development of the shippable Sungate coating. The abrasion resistance of the metallic Ti coating was, thus, significantly improved upon, as indicated by a number of abrasion resistance checks.

ATD Monthly Letter

Date: 3/25/93

Program Category:

Title/Project No.:

Department:

Authors: MA

Project Team:

Program Category:

Title/Project No.:

Department: Vacuum-Auto

Author: MA

Project Team:

* **Technical Highlights:** A representative set of Pastel samples from last month Evansville trial was exposed to Taber abrasion tests. The tests on the pre-heat samples confirmed our initial results regarding the significant role of impurity oxygen in increasing the abrasion resistance of titanium. Also, for Taber tests exceeding 300 cycles, post-heat experiments indicated a clear dependence of the coating abrasion resistance on its thickness: in general, increasing the thickness of the coating results in a higher after-heat haze. For fully oxidized films of 21 to 28 $\mu\text{g Ti/cm}^2$, coating abrasion at 1000 cycles corresponded to a 2.4% to 3.4% range of haze; in particular, the showed a 2.9% reading after 1000 cycles. These coatings will be further tested for environmental/chemical durability.

In addition to the Pastel sidelites reported previously, windshields consisting of one Pastel color were also fabricated during the past month. The single lites were coated in Evansville and shipped to Creighton for forming. During the bending process, the coating had to be on an outer surface to be fully oxidized. For process compatibility purposes, both the shipping and forming results were very encouraging.

ATD Monthly Letter

Date: 4/26/93

Program Category:

Department:

Title/Project No.:

Author: MA

Project Team:

Objective: The monolithic Pastel coatings, consisting of thermally oxidized Ti films, were subjected to a number of chemical durability tests. Also underway are experiments aiming to determine any unique, and thus patentable, features of the process, structure, and property relationships.

Technical Highlights: 1- the pastel coatings produced previously in Evansville were tested in boiling water for up to 8 hours. Coatings that were deposited with a finite flow of oxygen in the working gas (type II coatings) remained free of defects for the duration of the test. A few isolated post-boil defects on the films deposited in pure argon (type I coating) most likely originated from mechanical damage to these softer films prior to thermal oxidation.

The "SolarCool tests" including exposure to _____ were also performed. A typical Pastel coating passed all these tests with only minor alterations after exposure to _____. According to XRF measurements, the maximum titanium loss due to any one of the above chemical tests was about 1.3%, or less. In contrast, titanium oxide films deposited by the reactive sputtering method proved to be extremely reactive and, with the possible exception of _____, failed the SolarCool Tests.

Cleveland humidity tests are in progress for both before and after heat coatings including both types I and II films. Three of the samples including both of the heated as well as the before-heat type I films, have survived the test for a minimum of _____ days without significant visual and optical alterations. The before heat type II sample has developed a rather uniform goldish reflected color associated with an increased transmission. We believe this change to be due to the

2- XRD analyses of the above coatings have revealed important structural differences between the two film types (I&II). In the case of the as-deposited films, type I samples exhibit clear diffraction patterns characteristic of β -titanium. Type II coatings, however, appear to be mostly amorphous. This difference may be due to an oxygen-induced decrease in the mobility of the adsorbed metal atoms on the surface of the growing Ti films;

As reported last month, these metastable coatings are more _____ and, according to Taber abrasion measurements, _____

If the results of the above Cleveland test can be generalized, the non-equilibrium state of type II films may also explain _____

The initial crystallinity of the Ti films has a strong effect on the structure of the heated films as well. Although all of the above films crystallize in the _____ phase, the type II films show a strong preferential _____ In addition, XRD measurements indicate that the _____

Further work is in progress in order to determine if we can _____

ATD Monthly Letter

Date: 5/21/93

Program Category:

Title/Project No.:

Department:

Author:MA

Project Team:

* Technical Highlights: A 28-day Cleveland humidity test was completed for the pre- and post-heat Pastel coatings. The heated sample with as-deposited oxygen impurity, did not develop any discernible weathering defects during the above test. The coating with no initial oxygen impurity showed some degradation, probably at sites of earlier mechanical damage (i.e., scratches) to this softer coating, emphasizing the advantageous role of O₂ in hardening the pre-heat film.

Program Category:

Title/Project No.:

Department:

Author:MA

Project Team:

Nitrogen-induced amorphization in $\text{Al}_{80}\text{Ti}_{20}$ films prepared by reactive sputtering

Akihisa Inoue ^a, Hiroshi Yamagata ^b and Tsuyoshi Masumoto ^a

^a Institute for Materials Research, Tohoku University, Sendai 980, Japan

^b Research and Development Division, Yoshida Kogyo K.K., Kurobe, Toyama Pref. 938, Japan

Received 19 January 1993

A nitrogen-induced amorphization phenomenon was found to occur in an $\text{Al}_{80}\text{Ti}_{20}$ alloy prepared by sputtering in a flowing gas consisting of 0.98 Pa argon and 0.02 Pa nitrogen, though only an fcc phase is formed by sputtering in argon. The crystallization temperature and hardness increase from 662 to 728 K and 430 to 910, respectively, with an increase in the volume fraction of nitrogen from 2 to 7%.

It has recently been clarified [1-4] that an amorphous phase in Al-based systems is formed by rapid solidification. However, these amorphous alloys are limited to multicomponent alloy systems containing more than three components except for Al-Ln (Ln=lanthanide metal) binary alloys. There has been a strong demand for the formation of an amorphous phase in Al-based binary alloys without Ln element. We have carried out a systematic study on the formation and properties of Al-based binary amorphous alloys containing transition metal (TM) belonging to group IV to VIII as a solute element. Many trials of producing an amorphous phase in Al-TM alloys containing more than 80 at% Al were carried out by melt spinning and sputtering, but no amorphous single phase has been obtained. In the subsequent study on the formation of an amorphous phase in Al-based alloys, it was found that the dissolution of a small amount of nitrogen is very effective for the formulation of an amorphous phase in Al-rich composition ranges. This paper is intended to present the formation of amorphous films in $\text{Al}_{80}\text{Ti}_{20}$ by sputtering in an argon gas atmosphere containing a small amount of nitrogen, and their thermal stability and mechanical properties and to investigate the effect of the nitrogen-induced amorphization on their properties.

An $\text{Al}_{80}\text{Ti}_{20}$ (at%) alloy target with a disk shape of 75 mm in diameter and 6 mm in thickness was

prepared from pure Al with a purity of 99.99 mass% and pure Ti with a purity of 99.9 mass% by arc melting in a purified argon atmosphere. The premelted target was sputtered on a glass substrate to form a film with a surface shape of $50 \times 50 \text{ mm}^2$ and a thickness of about 1.3 mm using a dc magnetron sputtering apparatus. After evacuating the sputtering chamber mounted with the target material up to $6 \times 10^{-5} \text{ Pa}$, an argon gas or mixed argon and nitrogen gases of 1.0 Pa were fed through an automatic gas-flow controller to make argon plasma in the chamber. The partial pressure of nitrogen to argon plus nitrogen (P_N) was changed so as to be 0, 0.02, 0.04, 0.06, 0.07, 0.09 and 0.1 Pa. The argon plasma was generated between the substrate cathode and stainless-steel anode. The supplied anode current was usually 300 mA and the anode voltage was 0.45 kV. The sputtering time was adjusted to be 7.2 ks. Prior to sputtering target, the substrate was sputtered to clean its surface for 600 s by applying a negative bias against the substrate. The gap between the target and substrate was fixed at 60 mm. The analysis of the nitrogen element in the sputtered films was made by electron-probe microanalysis.

The as-prepared structures for the sputtered films were examined by thin-film type X-ray diffractometry using Cu K α radiation and transmission electron microscopy (TEM). The 2θ angle in the X-ray diffractometry was calibrated with Si powder. The

thin foils for TEM were prepared by cutting the sputtered film with a microtome. The crystallization temperature was measured at a heating rate of 0.33 K/s with a differential scanning calorimeter. Measurements of electrical conductivity were made at room temperature (≈ 290 K) by a conventional four-probe technique. Knoop hardness was examined by using a Vickers microhardness tester with a Knoop indenter and a load of 10 g.

Fig. 1 shows the change with P_N in the X-ray diffraction patterns of the sputtered $\text{Al}_{80}\text{Ti}_{20}$ films. The incident angle of the X-ray beam to the specimen surface was fixed to be 2.5° . Although the as-sputtered structure consists of an fcc phase at $P_N=0$ Pa, the increase of P_N to 0.02 Pa causes the structural change from an fcc to an amorphous phase. The formation of the amorphous phase is kept in the P_N range below 0.07 Pa and the further increase in P_N results in the formation of a mixed structure consisting of amorphous and hexagonal AlN. It is thus to be noticed that the mixing of a small amount of nitrogen in the sputtering atmosphere is very effective for the formation of an amorphous phase, indicating the achievement of nitrogen-induced amor-

phization in the Al-based alloy. Furthermore, it is seen in fig. 1 that the peak position in the broad diffraction peak revealing the formation of an amorphous phase shifts continuously to a lower-angle side with increasing P_N . Fig. 2 shows the change in the wave vector (K_p) at the peak position with P_N . K_p decreases almost linearly from 51.40 to 49.84 nm^{-1} in the P_N range 0.02–0.07 Pa and then more steeply in the higher P_N range. The linear decrease in K_p with P_N is thought to originate from the dissolution of nitrogen into the films. Also, the increase in the degree of the decrease in K_p around $P_N \approx 0.08$ Pa is presumably due to the structural change from an amorphous to an amorphous plus AlN phase.

In order to confirm the formation of the amorphous phase by the dissolution of nitrogen, TEM observations were carried out for the sputtered films prepared at $P_N=0$ and 0.02 Pa. Fig. 3 shows bright- and dark-field electron micrographs and a selected-area diffraction pattern of the $\text{Al}_{80}\text{Ti}_{20}$ film prepared at $P_N=0$ Pa. The diffraction rings shown in fig. 3b can be identified to be an fcc structure and the dark-field micrograph taken from the (111) reflection ring reveals that the fcc phase consists of very fine grains with a mean size of about 40 nm. Thus, no trace indicating the formation of an amorphous phase is seen in fig. 3. Fig. 4 shows a bright-field electron micro-

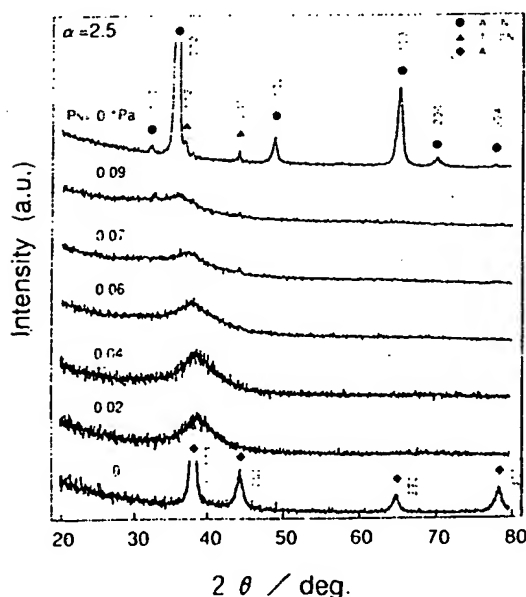


Fig. 1. X-ray diffraction patterns of the films prepared by sputtering an $\text{Al}_{80}\text{Ti}_{20}$ alloy in the atmospheres in which the P_N was changed to be 0, 0.02, 0.04, 0.06, 0.07, 0.09 and 0.1 Pa.

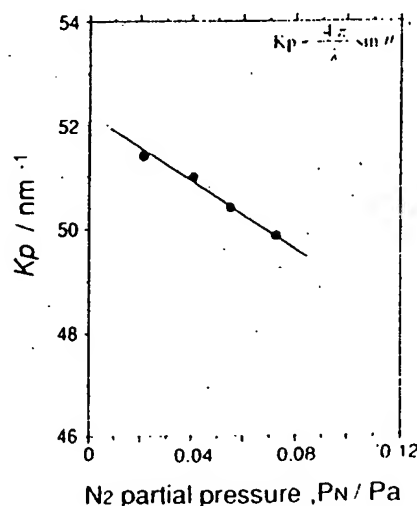


Fig. 2. Wave vector ($K_p = 4\pi / \lambda \sin \theta$) of the peak position of an amorphous halo in the X-ray diffraction patterns shown in fig. 1 as a function of P_N .

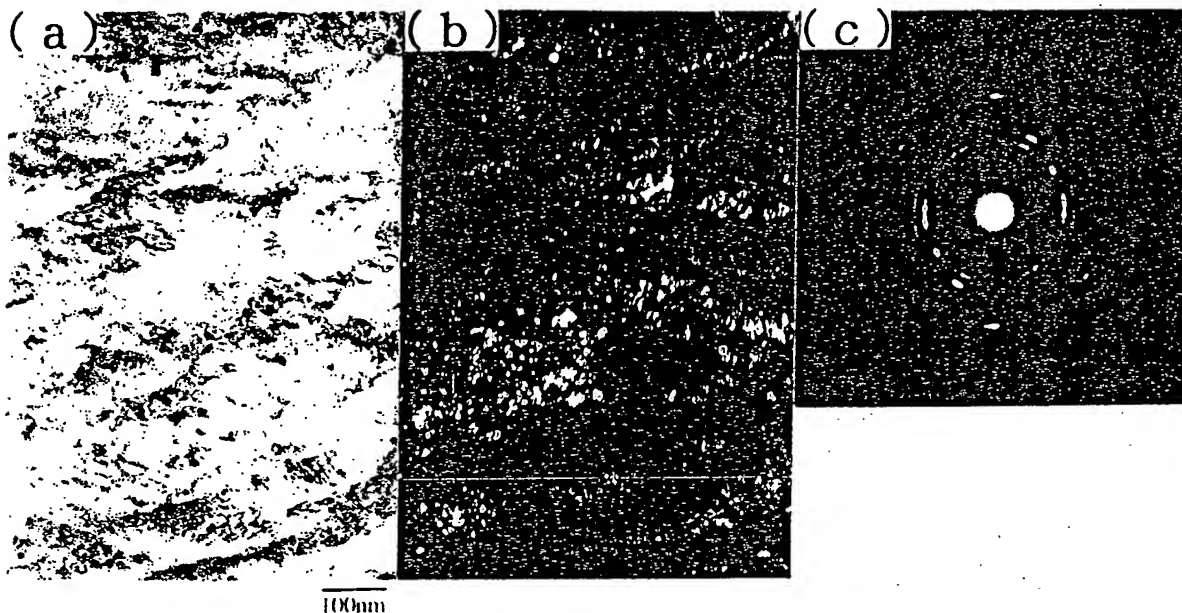


Fig. 3. Bright-field (a) and dark-field (b) electron micrographs and selected-area diffraction pattern (c) of an $\text{Al}_{60}\text{Ti}_{40}$ film prepared by sputtering at $P_N = 0$ Pa.

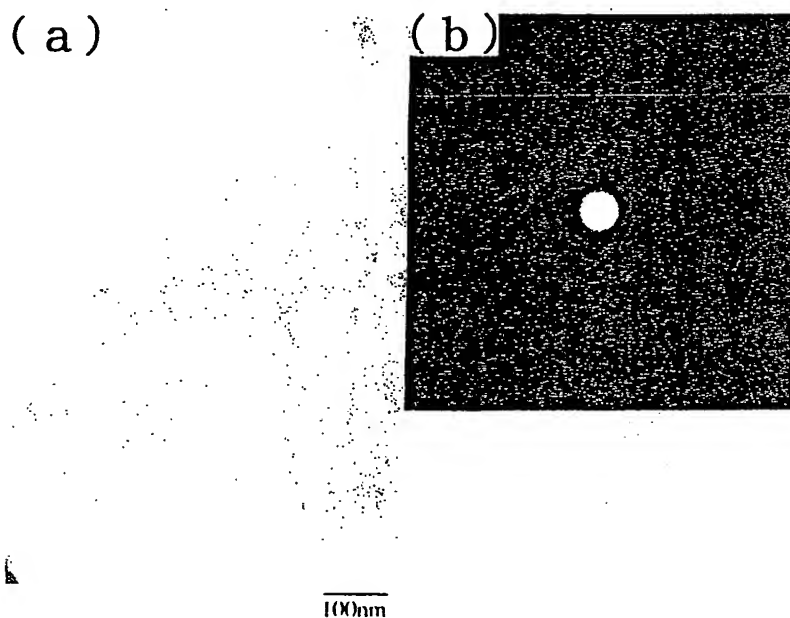


Fig. 4. Bright-field electron micrographs (a) and selected-area diffraction pattern (b) of an $\text{Al}_{60}\text{Ti}_{40}$ film prepared by sputtering at $P_N = 0.02$ Pa.

graph and a selected-area diffraction pattern of the sputtered $\text{Al}_{80}\text{Ti}_{20}$ film prepared at $P_N = 0.02$ Pa. No contrast revealing the existence of a crystalline phase is seen in the bright-field image and the diffraction pattern consists only of broad rings. The results shown in figs. 3 and 4 indicate clearly that the dissolution of nitrogen is very effective for the increase in the glass-forming ability for the Al-based alloys. This phenomenon can be regarded as nitrogen-induced amorphization.

It is expected that thermal stability and mechanical strength of the amorphous films change significantly with nitrogen content. Fig. 5 shows the changes with P_N in the onset temperature of crystallization (T_x) and the Knoop hardness number (H_K) of the sputtered amorphous $\text{Al}_{80}\text{Ti}_{20}$ films. As P_N increases from 0.02 to 0.07 Pa, T_x and H_K increase almost linearly from 662 to 728 K and from 51.40 to 49.84 nm^{-1} , respectively. This result indi-

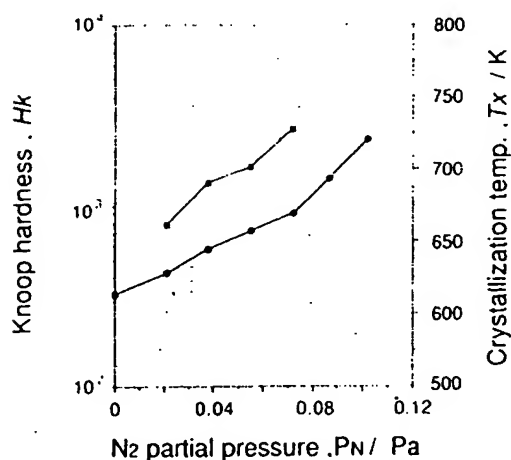


Fig. 5. Crystallization temperature (T_x) and Knoop hardness number (H_K) as a function of P_N for the amorphous $\text{Al}_{80}\text{Ti}_{20}$ films prepared by sputtering.

cates clearly that the dissolution of nitrogen is very effective for the increase in thermal stability and mechanical strength, in addition to the increase in the glass-forming ability. Furthermore, one can notice a close correlation between T_x or H_K and K_p from the data shown in figs. 2 and 5. It is therefore concluded that the changes in T_x and H_K for the amorphous films are dominated by the nitrogen content in the amorphous phase.

In conclusion, it was found that mixing of 2 vol% nitrogen to an argon sputtering atmosphere caused the formation of an amorphous single phase in an $\text{Al}_{80}\text{Ti}_{20}$ alloy, though only an fcc solid solution was formed in the film prepared by sputtering in an argon atmosphere. T_x and H_K increased from 662 to 728 K and from 430 to 910 with an increase in the partial pressure of nitrogen from 0.02 to 0.07 Pa. It is therefore concluded that the dissolution of nitrogen into the Al-based alloy is effective for the increase in the thermal stability and mechanical strength as well as for the increase in the glass-forming ability. The utilization of this concept is expected to bring about new amorphous Al-based alloys with better engineering properties in higher Al-concentration ranges.

References

- [1] A. Inoue, K. Ohtera and T. Masumoto, Sci. Rept. Res. Inst. Tohoku Univ. A 35 (1990) 115.
- [2] A. Inoue and T. Masumoto, in: Encyclopedia of materials science and engineering, Vol. 2, ed. R.W. Cahn (Pergamon Press, Oxford, 1990) p. 659.
- [3] A. Inoue and T. Masumoto, Mater. Sci. Eng. A 133 (1991) 6.
- [4] A. Inoue and T. Masumoto, Science and engineering of light metals, eds. K. Hirano, H. Oikawa and K. Ikeda (Japan Institut of Light Metals, Tokyo, 1991) p. 59.

EXHIBIT B

PPG INDUSTRIES, INC.

INTER-OFFICE CORRESPONDENCE

	DATE:	August 23, 1993
	FROM:	D. L. Seidel
TO: J. J. Finley M. Arbab	LOCATION:	Patent Department, 39 West
	SUBJECT:	TG-93-51 Category--Cathode Sputtered Coatings

This will acknowledge receipt of your disclosure dated August 6, 1993, and entitled "HARDENED METAL COATINGS BY MSVD PROCESSING."

Patent Department No. TG-93-51 has been assigned to this disclosure.

D. L. Seidel
D. L. Seidel
Assistant Patent Counsel
Glass

DLS/dmk



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No.: : 10/075,021
Applicants : James J. Finley and Mehran Arbab
Filed : February 12, 2002
Title : DURABLE SPUTTERED METAL OXIDE COATING
Group Art Unit : 1771
Examiner : Andrew T. Piziali

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. § 1.131

Sir:

I, James J Finley, hereby declare as follows:

1. Mehran Arbab and I are the named inventors of the invention described and claimed in the above-captioned application. I assigned all my rights, titles and interests in the above captioned application to PPG Industries, Inc. (hereinafter also referred to as "PPG"). Mr. Donald Lepiane, a retired employee of PPG, has informed me that the present assignee of the above-captioned application is PPG Industries Ohio, Inc, a wholly owned subsidiary of PPG.

2. In 1981 I began my employment with PPG, and during my employment with PPG, I have worked at its Glass Technology Center located in Harmarville, Pennsylvania, having various assignments relating to sputter coating on substrates, e.g. glass sheets. At the present time my title is "Senior Scientist" having responsibility for research, development and technology transfer of sputter-coated products.

3. On August 6, 1993, I signed a Memorandum of Invention entitled "HARDENED METAL COATINGS BY MSVD PROCESSING" having attachments thereto (hereinafter also referred to as "MOI") describing a concept conceived by Mehran Arbab and myself to sputter a metal in an atmosphere having reactive and non-reactive gases. The MOI

was forwarded to the Patent Department of PPG. The Memorandum of Invention form was one way I used to submit concepts I conceived relating to my work at PPG to the Patent Department of PPG to have the concept considered for a patent filing.

4. Attached Exhibit A is a copy of the MOI I signed on August 6, 1993, and was forwarded to the Patent Department of PPG. The attached copy of the MOI is redacted to omit dates prior to February 4, 1993, and/or PPG confidential information. Shortly after the MOI was forwarded to the Patent Department of PPG, I received an interoffice correspondence signed by Ms. Donna Seidel Assistant Patent Counsel for PPG advising me that the MOI was received and that Patent Department No. TG No. 93-51 was assigned to the disclosure. A copy of the interoffice correspondence I received having the signature of Ms. Donna Seidel is attached hereto as Exhibit B. Shortly after receiving the interoffice correspondence, I was advised that a patent application covering the concept disclosed in the MOI was filed.

5. I signed the MOI on August 6, 1993; however, the conception of the idea described under Section C Description of Invention of the MOI was had before February 5, 1993. More particularly, Section G of the MOI has the signature of Mr. Dennis Postupack a former employee of PPG acknowledging that the invention was disclosed to him in September 11 of a year prior to February 5, 1993. Data Book No. 6296 identified in Section I of the MOI is my Data Book and pages 33 and 34 of Exhibit A are copies of the pages of Data Book No. 6296 written by me and referenced in Section I of the MOI.

6. Pages 33 and 34 of Exhibit A show settings of a sputter coating apparatus to conduct experiments to collect information relating to the invention described in the MOI. As recorded on page 33 of my Data Book 6296, on September 11 of a year prior to February 5, 1993, titanium films, i.e. titanium metal films were sputtered under different conditions of cathode scanning speed and current for zero oxygen flow. On September 12 of a year prior to February 5, 1993, the invention described in Section C of the MOI was practiced by sputtering titanium films, i.e. titanium metal films in an atmosphere having different amounts of oxygen and argon. Listed under September 12 on attached page 33 of the Data Book are the operating conditions for three runs designated T-15, T-16 and T-17 in which a titanium metal film was sputtered in an atmosphere having oxygen and argon. The term "rate" means the deposition rate as determined from a crystal monitor in the coating

chamber. The flow rate of oxygen and argon are readings from flow rate instruments positioned outside the coater and do not indicate the percent of oxygen and argon in the coating chamber. The term "passes at" means the number of times the cathode at a set speed passed over the substrate being coated. The speed setting does not indicate the actual speed of the cathode. The % transmission of the coated substrate was measured while the coated substrate was in the coating chamber.

7. Exhibit A is a record that the conception of the invention was made and practiced before February 5, 1993.

8. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.


James J. Finley

8 - Apr - 05
Date

P MEMORANDUM OF INVENTION

Entry No. TG-93-51

To Patent Department -

AUG 18 1993

From (Location) HarmarvilleDisclosed herein for consideration is a record of invention as described below:

A. BRIEF TITLE OF INVENTION

Hardened metal coatings by MSVD processing

B. PURPOSE OF INVENTION

Metal coating is hardened during sputtering for subsequent use in shipping or processing, e. g., cold end, heat strengthening, bending and tempering.

C. DESCRIPTION OF INVENTION

Oxygen gas is bled into a vacuum system along with argon gas during the sputtering of a metal. The quantity of oxygen gas is kept at levels less than that required to switch from metal to oxide sputtering mode. The coating sputtered in this range of mixed argon/oxygen gas is only slightly higher in transmission than a coating sputtered only in argon, and the sputtering rate is approximately that of the metal. The amorphous metal coating produced using this method is significantly harder than the crystalline metal coating produced by sputtering in pure argon gas. Higher oxygen/argon gas ratios produce a harder coatings. This coating could be heated to produce a haze free, dense, crystalline metal oxide coating with first surface durability. This is an extremely cost effective way to produce thick metal oxide coatings with applications as interference color coatings with selected chromas. Oxygen is the preferred gas; nitrogen has the same effect, however, the heated coating is extremely hazy. The preferred metals are titanium and zirconium. Other metals include Al, Hf, Nb and V.

Attach supplemental sheets as necessary.


D. LIST PERTINENT PATENTS OR PUBLICATIONS KNOWN TO YOU

A. Inove, H. Vamagata & T. Masumoto; Nitrogen-Induced Amorphization in Al80Ti20 Films Prepared by Reactive Sputtering; Materials Letters 16 (1993), pages 181-184


NOTE: IN SECTIONS E, G, AND L, PLEASE TYPE OR PRINT NAMES ADJACENT ALL SIGNATURES.

E. WITNESS TO FOREGOING DESCRIPTION AND TO THE SIGNATURE(S)
OF INVENTOR(S)

SIGNATURE OF INVENTOR(S)

8/6/93
DATEAugust 6, 1993
DATEJohn D. Basil
TYPE OR PRINTJames J. Finley
TYPE OR PRINT_____
DATE

DATE

August 6, 1993
DATE_____
TYPE OR PRINTMehran Arbab
TYPE OR PRINT

IMPORTANT: If there is any record of the invention preceding the date of this memo, please fill in the appropriate data on the reverse hereof.

F. WHEN DID THE INVENTION FIRST OCCUR TO YOU (GIVE DATE)

Sept 11,

G. WHEN AND TO WHOM, OTHER THAN THE CO-INVENTORS, DID YOU FIRST COMMUNICATE THE INVENTION (GIVE DATE)

D.S. Postupack, Sept 11,

I (WE) ACKNOWLEDGE THAT THE INVENTION WAS COMMUNICATED TO ME (US) ON THE DATE INDICATED ABOVE.

SIGNED

Dennis S. Postupack

TYPE OR PRINT

DENNIS. POSTUPACK

SIGNED

TYPE OR PRINT

H. WHEN AND WHERE WAS THE FIRST SKETCH, DRAWING, OR PHOTOGRAPH, IF ANY, MADE OF THE INVENTION. IDENTIFY AND ATTACH COPY.

I. WHEN WAS THE INVENTION FIRST DESCRIBED IN WRITING. GIVE DATE AND IDENTIFY NOTEBOOK, REPORT OR OTHER SOURCE. ATTACH COPY.

Sept 11, Data Book No. 6296 pages

J. IDENTIFY PERTINENT DESCRIPTIONS, REPORTS, SUMMARIES, DRAWINGS, PHOTOGRAPHS, ETS. SUBSEQUENT TO I ABOVE.

VET036 sample series deposition parameters, Wks 28 Line 8, February 5, 1993

Test results for Taber abrasion analysis of the above samples, March 22, 1993

Plant trial notes, Mehran Arbab, February 4 & 5, 1993

K. WHEN (GIVE DATE) AND WHERE WAS THE INVENTION EITHER FIRST MADE (MACHINE OR PRODUCT), OR FIRST PERFORMED (PROCESS)

Sept 11,

L. WHEN AND BY WHOM WAS THE INVENTION FIRST TESTED ANYWHERE FOR PERFORMANCE (GIVE DATE, AND NAMES OF OBSERVERS)

Sept 11, P.S. Postupack

I (WE) ACKNOWLEDGE THAT I (WE) OBSERVED THE PERFORMANCE TEST ON THE DATE INDICATED ABOVE.

SIGNED

TYPE OR PRINT

SIGNED

TYPE OR PRINT

M. HAS THE INVENTION BEEN PUBLISHED OR COMMUNICATED OUTSIDE THE COMPANY (GIVE DETAILS)

no

N. IF A PRODUCT RESULTING FROM THE INVENTION HAS BEEN USED OR SOLD ANYWHERE, STATE WHEN AND WHERE

End of year - windshields and sidelights (not oxidized) were sent to GM; - Samples of oxidized coatings were shown to GM, Chrysler, Toyota

TITLE

DATE

Tues, Sept 11

Sputter Ti films under different conditions of cathode scanning speed and current for TiO_2 in oxygen flow

Ti-12 Current-15; scan-max Rate 35 7 passes to 10.5%
abrasion resistance is VG

Ti-13 Current-15 scan-max Rate 35 4 passes to 8.4%
abrasion resistance is POOR

Ti-14 Current-10; scan-max Rate 20 11 passes to 10.1%
abrasion res VG

I took pictures of Ag splot on the (res) time since splot is

Wed, Sept 12

Sputter Ti films also at 15 amps and scan of 6 with different amounts of O_2

Ti-15 Rate 36; O_2 flow 9 Ar flow 18; 8 passes at "6" and 1 pass at "8" to 9.4% T. abrasion res Excellent. Reflectance is brownish

Ti-16 Rate 36; O_2 flow 4.5 Ar flow 18.4; 5 passes at "6" to 9.2% T. abrasion res - Excellent; reflectance is slight brownish, between metallic and Ti-15 ref.

Ti-17 Rate 36; O_2 flow 1.5; 5 passes 9.0% T abrasion excellent

Thurs, Sept 13

Sputter Ti in N_2

Ti-18 (Sputtered 9-12) Pure Argon (no O_2 or N_2)
abrasion resistance POOR

EXPERIMENT CONDUCTED BY

DATE

WITNESSED BY

DATE

TITLE _____

DATE _____

Ti-19 Rate (17-18); N_2 flow 10.5 (Scope A-ball SS)
 12 passes to 22.4 %T; Abrasion Res - Ajax excellent
 Prunice-poor; Bronze ref.

Ti-20 Rate 33; N_2 flow 5* (+ half ball); 8 passes,
 10% T; Excellent abrasion resistance for
 both Ajax and Prunice!; Goldish reflectance
 $R = 46.0/58$

Ti-21 Rate 35; N_2 flow 1.5; 5 passes to 8.5% T;
 Abrasion - Ajax VVG, Prunice VVG. $R = 85.2/58$

Ti-22 Rate 27-28; N_2 flow 3.5, O_2 flow 2.5; 14 passes
 10.7% T

Fri, Sept 14

Try glass cleaned in washer (covered)

Ti-23 Rate 35; O_2 flow - 1.5; 5 passes to 8.7% T
 Abrasion res VG

~~RECALL~~ Try glass CeO₂ polished but NO cover

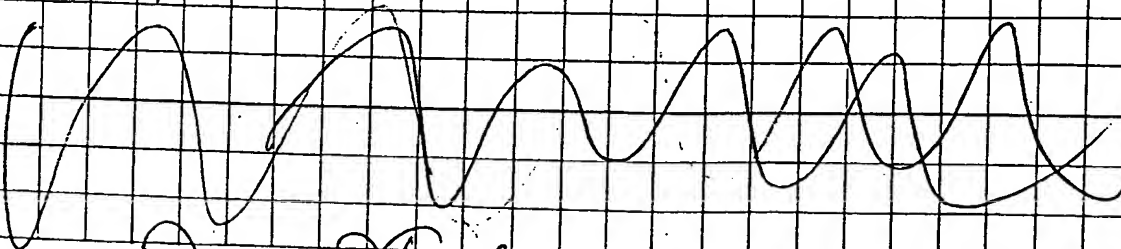
Ti-24 Rate 35; O_2 flow - 1.5; 5 passes, 7.7% T
 Abrasion res VG

Look at #1503 (Br/Sr 70 - $As_2 - (Zr/Sr)_2O$ film
 under optical. Also no spots, defects etc.

Mon Sept 17 to Wed Sept 27

Wardshields for GM coated with Ti

I will give details after project
 is completed



EXPERIMENT CONDUCTED BY

James J. Smith
 Sept 24,

DATE

WITNESSED BY _____

DATE _____

2655cm) = -14 + 1.7 Amps

Feb 4, 93

Ken Schoeffner (Tech coord. for 1-8.)
Paul Duff (Prod. coordinator)

(419) 666-7068

USAF 12:00 12:38

585

Delta 7:00 8:05 C.M. 8:55 to mil. 9:35

Northwest 7:35 8:39 Detroit 9:25 to mil : 9:32

Milwaukee 5:55 to Pitt 8:14 PM

Northwest 1:40

6:7m Pitt

AT 8:16 PM

*

610 ± 28 ug

The color of the pastel sample was measured on 6 disp. spots & it appears to correspond to the 610 Å thickness sample with some color points at lower thickness (the top side, which suggests thickness gradient of the 8" x 12") (8590 ± $\frac{1}{4}$ film at 2.3)

Let's run between 517 Å (12 buses) & 655 Å (10 KVP) at 1 PWS. Inter. val. w/ 5 cathodes at 75° iPM:

517 → 23 ug/cm² : 1.14 = 20 Q times 2 or 5!

610 → 28 ug/cm² : 1.14 = 25

22 Å / MP

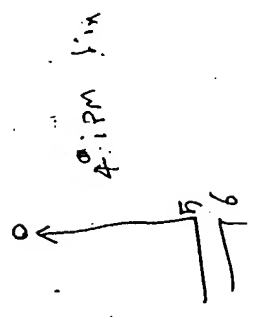
22.2 $\frac{150 \text{ iPM, scat}}{1.14 \text{ ug/cm}^2} \Rightarrow \sim 19.5 \text{ Amps/ug}$
 1 517 Å $\Rightarrow \frac{4500 \text{ Amps}}{4500 \text{ Amps}} \Rightarrow 75 \text{ iPM, 5 cathodes}$
 2 557 Å $\Rightarrow \frac{4500 \text{ Amps}}{4500 \text{ Amps}} \Rightarrow 45 \text{ Amps/cathode}$
 3 597 Å $\Rightarrow 529 \text{ Amps}$
 + 635 Å $\Rightarrow 563 \text{ Amps}$

*

Also try the Zn Sn!

2-5-93

VET036
35
38
41
44



VET036

5:18 PM

*

Sample no	AmH (g?)	Q ₂ N	Q	Y
VET 2	38 (40)	0.007		
6	43	0.2227	0.1745	10.42
7	39	0.3139	0.2359	11.70
8	37	0.3795	0.3310	11.11
9	38	0.3545	0.2924	14.22
10	40	0.2912	0.2151	10.39
11	41	0.2655	0.1884	10.15
12 (49, 4m)	38			
13	40.5			

Creighton windshields: 12

6: at 42.4

8: at 40.5

4mm side 1:10

27 at 40.5 (3) stuck 23/30x2 4' sample 1
 9 at 48.5 (40.5) stuck 67/30x2 2' sample 1
 9 at 44. blue stuck 47/30x2 2' sample 1
 9 at 39 (47) stuck 67/30x2 2' sample 1

Run ILS for 13

* 520-1 Cherry Blazer f.D. 8
Line 4

1 1 0

More than fifty 4mm side-lites (clear, 520-1 pattern) were coated with 4 Ti thicknesses targeting 4 different color coordinates. These samples were subsequently tempered on line 28-4 (W. Zimmerman). Presumably as a result of the undefined heat pattern (too few samples were available), all of the lites developed varying degrees of near-edge crazing. This issue, as well as the unknown effects of cold end processing of the coated substrate (i.e., cutting, edging, and washing) remain to be resolved.

ATD Monthly Letter

Date: 12/21/

Program Category:

Department:

Title/Project No.:

Author: MA

ATD Monthly Letter

Date: 2/22/93

Program Category:

Title/Project No.:

Department:

Authors:MA

Project Team:

Program Category:

Title/Project No.:

Department:Vacuum-Auto

Author:MA

Project Team:

* **Technical Highlights:** A one day trial at wks 28-8 was dedicated to a preliminary evaluation of fabrication of the monolithic, high transmission, colored coatings. This trial was based on the Pastel concept developed at the lab. (JJ Finley), where an opaque metallic Ti (or other metals or alloys) deposited on glass, is oxidized during the tempering (or bending) process. Depending on its thickness, the resulting oxide layer imparts a variety of reflective colors to the glazing. The reason for the deposition of the initial coating in the metallic mode is to exploit its high deposition rate (as compared to the reactive sputtering of, e.g., TiO_2) and to make the Pastel concept cost effective and compatible with the existing coater capabilities. The concern with this approach is, however, the mechanical durability of the metallic titanium coating.

With the help of an xy color chart generated from the laboratory samples, a specific target color (ca. $x=0.2782$, $y=0.2028$) was obtained in a short period of time. However, during this trial, we concentrated only on samples cut from the center of the coated lites; that is, the potentially significant gradient problems were not examined.

The concern about mechanical durability of the metallic coating was addressed using the partial oxidation concept similar to that used in the development of the shippable Sungate coating. The abrasion resistance of the metallic Ti coating was, thus, significantly improved upon, as indicated by a number of abrasion resistance checks.

ATD Monthly Letter

Date: 3/25/93

Program Category:

Title/Project No.:

Department:

Authors:MA

Project Team:

Program Category:

Title/Project No.:

Department: Vacuum-Auto

Author:MA

Project Team:

* Technical Highlights: A representative set of Pastel samples from last month Evansville trial was exposed to Taber abrasion tests. The tests on the pre-heat samples confirmed our initial results regarding the significant role of impurity oxygen in increasing the abrasion resistance of titanium. Also, for Taber tests exceeding 300 cycles, post-heat experiments indicated a clear dependence of the coating abrasion resistance on its thickness: in general, increasing the thickness of the coating results in a higher after-heat haze. For fully oxidized films of 21 to 28 $\mu\text{g Ti/cm}^2$, coating abrasion at 1000 cycles corresponded to a 2.4% to 3.4% range of haze; in particular, the showed a 2.9% reading after 1000 cycles. These coatings will be further tested for environmental/chemical durability.

In addition to the Pastel sidelites reported previously, windshields consisting of one Pastel color were also fabricated during the past month. The single lites were coated in Evansville and shipped to Creighton for forming. During the bending process, the coating had to be on an outer surface to be fully oxidized . For process compatibility purposes, both the shipping and forming results were very encouraging.

ATD Monthly Letter

Date: 4/26/93

Program Category:

Department:

Title/Project No.:

Author: MA

Project Team:

Objective: The monolithic Pastel coatings, consisting of thermally oxidized Ti films, were subjected to a number of chemical durability tests. Also underway are experiments aiming to determine any unique, and thus patentable, features of the process, structure, and property relationships.

Technical Highlights: 1- the pastel coatings produced previously in Evansville were tested in boiling water for up to 8 hours. Coatings that were deposited with a finite flow of oxygen in the working gas (type II coatings) remained free of defects for the duration of the test. A few isolated post-boil defects on the films deposited in pure argon (type I coating) most likely originated from mechanical damage to these softer films prior to thermal oxidation.

The "SolarCool tests" including exposure to _____ were also performed. A typical Pastel coating passed all these tests with only minor alterations after exposure to _____. According to XRF measurements, the maximum titanium loss due to any one of the above chemical tests was about 1.3%, or less. In contrast, titanium oxide films deposited by the reactive sputtering method proved to be extremely reactive and, with the possible exception of _____, failed the SolarCool Tests.

Cleveland humidity tests are in progress for both before and after heat coatings including both types I and II films. Three of the samples including both of the heated as well as the before-heat type I films, have survived the test for a minimum of _____ days without significant visual and optical alterations. The before heat type II sample has developed a rather uniform goldish reflected color associated with an increased transmission. We believe this change to be due to the

2- XRD analyses of the above coatings have revealed important structural differences between the two film types (I&II). In the case of the as-deposited films, type I samples exhibit clear diffraction patterns characteristic of β -titanium. Type II coatings, however, appear to be mostly amorphous. This difference may be due to an oxygen-induced decrease in the mobility of the adsorbed metal atoms on the surface of the growing Ti films;

As reported last month, these metastable coatings are more _____ and, according to Taber abrasion measurements, _____

If the results of the above Cleveland test can be generalized, the non-equilibrium state of type II films may also explain _____

The initial crystallinity of the Ti films has a strong effect on the structure of the heated films as well. Although all of the above films crystallize in the _____ phase, the type II films show a strong preferential _____ In addition, XRD measurements indicate that the _____

Further work is in progress in order to determine if we can _____

ATD Monthly Letter

Date: 5/21/93

Program Category:

Title/Project No.:

Department:

Author:MA

Project Team:

* Technical Highlights: A 28-day Cleveland humidity test was completed for the pre- and post-heat Pastel coatings. The heated sample with as-deposited oxygen impurity, did not develop any discernible weathering defects during the above test. The coating with no initial oxygen impurity showed some degradation, probably at sites of earlier mechanical damage (i.e., scratches) to this softer coating, emphasizing the advantageous role of O₂ in hardening the pre-heat film.

Program Category:

Title/Project No.:

Department:

Author:MA

Project Team:

Nitrogen-induced amorphization in $\text{Al}_{80}\text{Ti}_{20}$ films prepared by reactive sputtering

Akihisa Inoue ^a, Hiroshi Yamagata ^b and Tsuyoshi Masumoto ^a

^a Institute for Materials Research, Tohoku University, Sendai 980, Japan

^b Research and Development Division, Yoshida Kogyo K.K., Kurobe, Toyama Pref. 938, Japan

Received 19 January 1993

A nitrogen-induced amorphization phenomenon was found to occur in an $\text{Al}_{80}\text{Ti}_{20}$ alloy prepared by sputtering in a flowing gas consisting of 0.98 Pa argon and 0.02 Pa nitrogen, though only an fcc phase is formed by sputtering in argon. The crystallization temperature and hardness increase from 662 to 728 K and 430 to 910, respectively, with an increase in the volume fraction of nitrogen from 2 to 7%.

It has recently been clarified [1-4] that an amorphous phase in Al-based systems is formed by rapid solidification. However, these amorphous alloys are limited to multicomponent alloy systems containing more than three components except for Al-Ln (Ln=lanthanide metal) binary alloys. There has been a strong demand for the formation of an amorphous phase in Al-based binary alloys without Ln element. We have carried out a systematic study on the formation and properties of Al-based binary amorphous alloys containing transition metal (TM) belonging to group IV to VIII as a solute element. Many trials of producing an amorphous phase in Al-TM alloys containing more than 80 at% Al were carried out by melt spinning and sputtering, but no amorphous single phase has been obtained. In the subsequent study on the formation of an amorphous phase in Al-based alloys, it was found that the dissolution of a small amount of nitrogen is very effective for the formulation of an amorphous phase in Al-rich composition ranges. This paper is intended to present the formation of amorphous films in $\text{Al}_{80}\text{Ti}_{20}$ by sputtering in an argon gas atmosphere containing a small amount of nitrogen, and their thermal stability and mechanical properties and to investigate the effect of the nitrogen-induced amorphization on their properties.

An $\text{Al}_{80}\text{Ti}_{20}$ (at%) alloy target with a disk shape of 75 mm in diameter and 6 mm in thickness was

prepared from pure Al with a purity of 99.99 mass% and pure Ti with a purity of 99.9 mass% by arc melting in a purified argon atmosphere. The premelted target was sputtered on a glass substrate to form a film with a surface shape of $50 \times 50 \text{ mm}^2$ and a thickness of about 1.3 mm using a dc magnetron sputtering apparatus. After evacuating the sputtering chamber mounted with the target material up to $6 \times 10^{-5} \text{ Pa}$, an argon gas or mixed argon and nitrogen gases of 1.0 Pa were fed through an automatic gas-flow controller to make argon plasma in the chamber. The partial pressure of nitrogen to argon plus nitrogen (P_N) was changed so as to be 0, 0.02, 0.04, 0.06, 0.07, 0.09 and 0.1 Pa. The argon plasma was generated between the substrate cathode and stainless-steel anode. The supplied anode current was usually 300 mA and the anode voltage was 0.45 kV. The sputtering time was adjusted to be 7.2 ks. Prior to sputtering target, the substrate was sputtered to clean its surface for 600 s by applying a negative bias against the substrate. The gap between the target and substrate was fixed at 60 mm. The analysis of the nitrogen element in the sputtered films was made by electron-probe microanalysis.

The as-prepared structures for the sputtered films were examined by thin-film type X-ray diffractometry using $\text{Cu K}\alpha$ radiation and transmission electron microscopy (TEM). The 2θ angle in the X-ray diffractometry was calibrated with Si powder. The

thin foils for TEM were prepared by cutting the sputtered film with a microtome. The crystallization temperature was measured at a heating rate of 0.33 K/s with a differential scanning calorimeter. Measurements of electrical conductivity were made at room temperature (≈ 290 K) by a conventional four-probe technique. Knoop hardness was examined by using a Vickers microhardness tester with a Knoop indenter and a load of 10 g.

Fig. 1 shows the change with P_N in the X-ray diffraction patterns of the sputtered $\text{Al}_{80}\text{Ti}_{20}$ films. The incident angle of the X-ray beam to the specimen surface was fixed to be 2.5° . Although the as-sputtered structure consists of an fcc phase at $P_N=0$ Pa, the increase of P_N to 0.02 Pa causes the structural change from an fcc to an amorphous phase. The formation of the amorphous phase is kept in the P_N range below 0.07 Pa and the further increase in P_N results in the formation of a mixed structure consisting of amorphous and hexagonal AlN. It is thus to be noticed that the mixing of a small amount of nitrogen in the sputtering atmosphere is very effective for the formation of an amorphous phase, indicating the achievement of nitrogen-induced amor-

phization in the Al-based alloy. Furthermore, it is seen in fig. 1 that the peak position in the broad diffraction peak revealing the formation of an amorphous phase shifts continuously to a lower-angle side with increasing P_N . Fig. 2 shows the change in the wave vector (K_p) at the peak position with P_N . K_p decreases almost linearly from 51.40 to 49.84 nm^{-1} in the P_N range 0.02–0.07 Pa and then more steeply in the higher P_N range. The linear decrease in K_p with P_N is thought to originate from the dissolution of nitrogen into the films. Also, the increase in the degree of the decrease in K_p around $P_N \approx 0.08$ Pa is presumably due to the structural change from an amorphous to an amorphous plus AlN phase.

In order to confirm the formation of the amorphous phase by the dissolution of nitrogen, TEM observations were carried out for the sputtered films prepared at $P_N=0$ and 0.02 Pa. Fig. 3 shows bright- and dark-field electron micrographs and a selected-area diffraction pattern of the $\text{Al}_{80}\text{Ti}_{20}$ film prepared at $P_N=0$ Pa. The diffraction rings shown in fig. 3b can be identified to be an fcc structure and the dark-field micrograph taken from the (111) reflection ring reveals that the fcc phase consists of very fine grains with a mean size of about 40 nm. Thus, no trace indicating the formation of an amorphous phase is seen in fig. 3. Fig. 4 shows a bright-field electron micro-

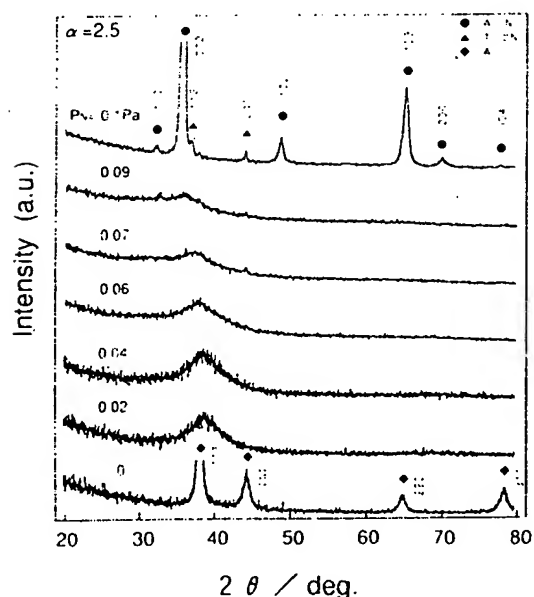


Fig. 1. X-ray diffraction patterns of the films prepared by sputtering an $\text{Al}_{80}\text{Ti}_{20}$ alloy in the atmospheres in which the P_N was changed to be 0, 0.02, 0.04, 0.06, 0.07, 0.09 and 0.1 Pa.

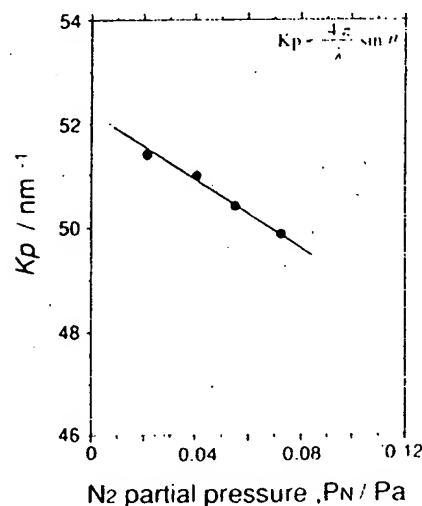


Fig. 2. Wave vector ($K_p = 4\pi / \lambda \sin \theta$) of the peak position of an amorphous halo in the X-ray diffraction patterns shown in fig. 1 as a function of P_N .

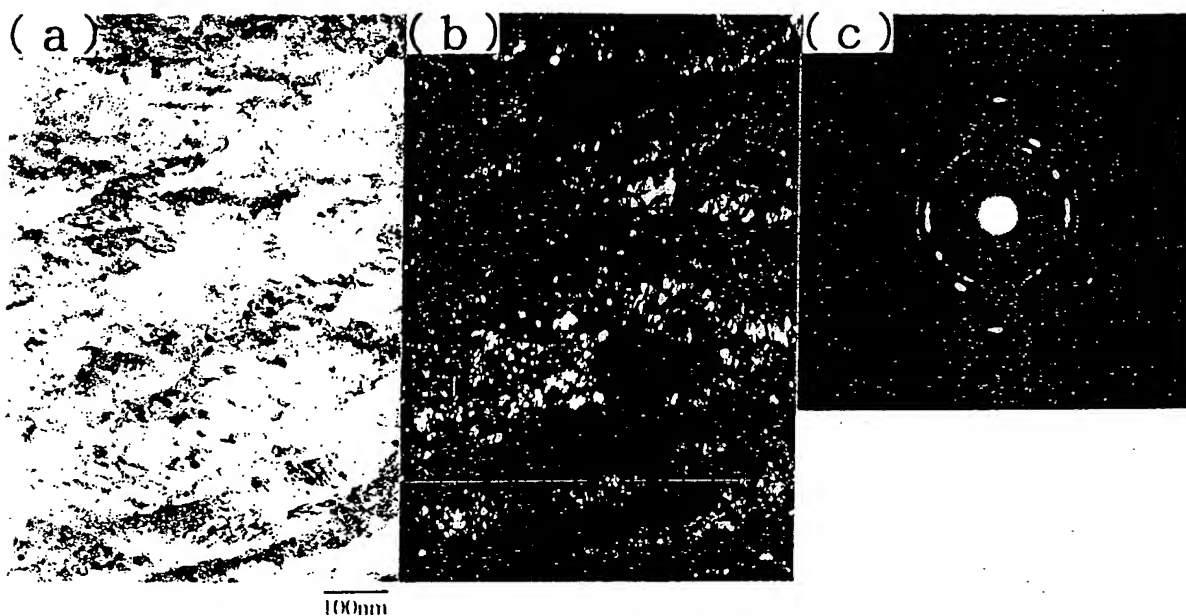


Fig. 3. Bright-field (a) and dark-field (b) electron micrographs and selected-area diffraction pattern (c) of an $\text{Al}_{60}\text{Ti}_{20}$ film prepared by sputtering at $P_N = 0$ Pa.

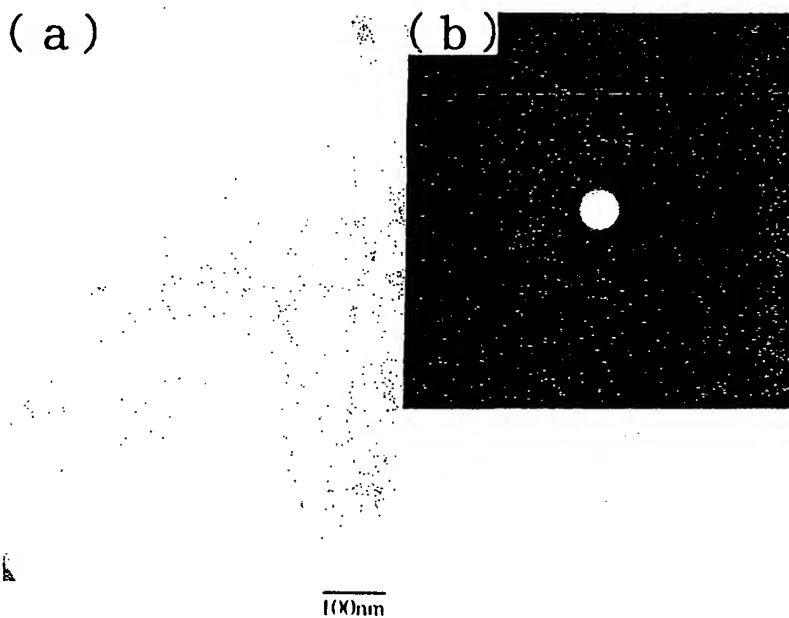


Fig. 4. Bright-field electron micrographs (a) and selected-area diffraction pattern (b) of an $\text{Al}_{60}\text{Ti}_{20}$ film prepared by sputtering at $P_N = 0.02$ Pa.

graph and a selected-area diffraction pattern of the sputtered $\text{Al}_{80}\text{Ti}_{20}$ film prepared at $P_N = 0.02$ Pa. No contrast revealing the existence of a crystalline phase is seen in the bright-field image and the diffraction pattern consists only of broad rings. The results shown in figs. 3 and 4 indicate clearly that the dissolution of nitrogen is very effective for the increase in the glass-forming ability for the Al-based alloys. This phenomenon can be regarded as nitrogen-induced amorphization.

It is expected that thermal stability and mechanical strength of the amorphous films change significantly with nitrogen content. Fig. 5 shows the changes with P_N in the onset temperature of crystallization (T_x) and the Knoop hardness number (H_K) of the sputtered amorphous $\text{Al}_{80}\text{Ti}_{20}$ films. As P_N increases from 0.02 to 0.07 Pa, T_x and H_K increase almost linearly from 662 to 728 K and from 51.40 to 49.84 nm^{-1} , respectively. This result indi-

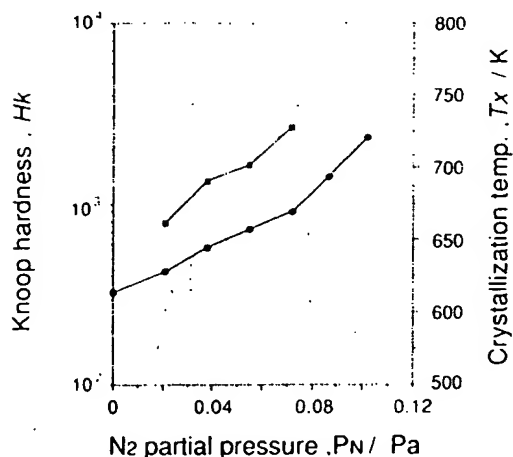


Fig. 5. Crystallization temperature (T_x) and Knoop hardness number (H_K) as a function of P_N for the amorphous $\text{Al}_{80}\text{Ti}_{20}$ films prepared by sputtering.

cates clearly that the dissolution of nitrogen is very effective for the increase in thermal stability and mechanical strength, in addition to the increase in the glass-forming ability. Furthermore, one can notice a close correlation between T_x or H_K and K_p from the data shown in figs. 2 and 5. It is therefore concluded that the changes in T_x and H_K for the amorphous films are dominated by the nitrogen content in the amorphous phase.

In conclusion, it was found that mixing of 2 vol% nitrogen to an argon sputtering atmosphere caused the formation of an amorphous single phase in an $\text{Al}_{80}\text{Ti}_{20}$ alloy, though only an fcc solid solution was formed in the film prepared by sputtering in an argon atmosphere. T_x and H_K increased from 662 to 728 K and from 430 to 910 with an increase in the partial pressure of nitrogen from 0.02 to 0.07 Pa. It is therefore concluded that the dissolution of nitrogen into the Al-based alloy is effective for the increase in the thermal stability and mechanical strength as well as for the increase in the glass-forming ability. The utilization of this concept is expected to bring about new amorphous Al-based alloys with better engineering properties in higher Al-concentration ranges.

References

- [1] A. Inoue, K. Ohtera and T. Masumoto, Sci. Rept. Res. Inst. Tohoku Univ. A 35 (1990) 115.
- [2] A. Inoue and T. Masumoto, in: Encyclopedia of materials science and engineering, Vol. 2, ed. R.W. Cahn (Pergamon Press, Oxford, 1990) p. 659.
- [3] A. Inoue and T. Masumoto, Mater. Sci. Eng. A 133 (1991) 6.
- [4] A. Inoue and T. Masumoto, Science and engineering of light metals, eds. K. Hirano, H. Oikawa and K. Ikeda (Japan Institute of Light Metals, Tokyo, 1991) p. 59.

EXHIBIT B

PPG INDUSTRIES, INC.

INTER-OFFICE CORRESPONDENCE

	DATE:	August 23, 1993
	FROM:	D. L. Seidel
TO: J. J. Finley M. Arbab	LOCATION:	Patent Department, 39 West
	SUBJECT:	TG-93-51 Category--Cathode Sputtered Coatings

This will acknowledge receipt of your disclosure dated August 6, 1993, and entitled "HARDENED METAL COATINGS BY MSVD PROCESSING."

Patent Department No. TG-93-51 has been assigned to this disclosure.

D. L. Seidel
D. L. Seidel
Assistant Patent Counsel
Glass

DLS/dmk



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No.: : 10/075,021
Applicants : James J. Finley and Mehran Arbab
Filed : February 12, 2002
Title : DURABLE SPUTTERED METAL OXIDE COATING
Group Art Unit : 1771
Examiner : Andrew T. Piziali

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. § 1.131

Sir:

I, Donald C. Lepiane, hereby declare as follows:

1. I am a Patent Attorney registered to practice before the United States Patent and Trademark Office. I have been assigned Registration No. 25,996.

2. In 1972 I was hired by PPG Industries, Inc. (hereinafter also referred to as "PPG") and during my employment with PPG worked in the Patent Department (later named "Intellectual Property Department") of PPG. In 2001, I retired from PPG, and since my retirement, I have been a consultant to PPG working in the area of filing and prosecuting patent applications before Patent Offices of various countries.

3. From 1982 to my retirement, I had responsibility for worldwide intellectual property matters of the Flat Glass Business Units of PPG. My responsibilities included receiving concepts and/or ideas from employees of PPG, assigning them to Patent Attorneys reporting to me to determine if patent applications should be filed, and making certain patent applications were timely filed and prosecuted. Many of the ideas were submitted to the Patent Department of PPG on Memorandum of Invention forms. During my employment with PPG, it was the practice of the Patent Department of PPG to stamp Memorandum of Inventions with the date they were received on the date they were received,

and thereafter a Patent Department No. assigned to the Memorandum of Invention was typed or written on the Memorandum of Invention.

4. On August 18, 1993, a Memorandum of Invention entitled "HARDENED METAL COATINGS BY MSVD PROCESSING" having attachments thereto (hereinafter also referred to as "MOI") describing an invention of James J. Finley and Mehran Arbab to sputter a metal in an atmosphere having reactive and non-reactive gases was received by the Patent Department of PPG. After the MOI was stamped with the date of August 18, 1993, and the assigned Patent Department No. typed on the MOI, it was forwarded to me.

6. Attached Exhibit A is a copy of the MOI redacted by me to remove dates prior to February 4, 1993; writings relating to matters other than the invention described in Section C of the MOI, and/or PPG confidential information.

7. After I reviewed and studied the MOI, I assigned it to Ms. Donna Seidel (see initials "DLS" I wrote in the upper right hand corner of Exhibit A). An inter office correspondence acknowledging receipt of the MOI and identifying the assigned Patent Department No. was sent to James J. Finley and Mehran Arbab by Ms. Donna Seidel. I base the preceding statement on the copy of the inter office correspondence attached hereto as Exhibit B.

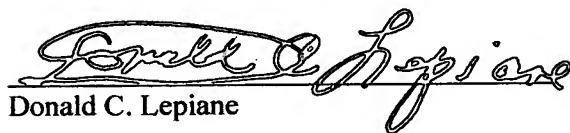
8. From 1982 to my retirement from PPG, Patent Attorneys reporting to me, managers of the technical center at Harmarville, submitters of the concepts and/or ideas and I periodically reviewed submitted concepts and/or ideas to assign filing priority ratings. After the submitted concepts and/or ideas were rated, each Patent Attorney reporting to me would make a filing priority list.

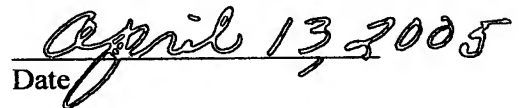
9. I recently made a study of the files of PPG. The study showed that U.S. Patent Application Serial No. 08/151,229 filed on November 12, 1993, in the names of James J. Finley and Mehran Arbab for "DURABLE SPUTTER METAL OXIDE COATING" discloses and claims the subject matter of the MOI (Exhibit A). Based on the fact that the MOI was received by the Patent Department of PPG on August 18, 1993, and a patent application was filed on November 12, 1993, (less than three months after the MOI was received by the Patent Department), I conclude that the MOI that the MOI was assigned a high filing priority and was processed accordingly.

10. The study of the files of PPG further shows that the above identified U.S. Patent Application Serial No. 10/075,021 filed February 12, 2002, is a divisional of U.S. Patent Application Serial No. 08/508,408 filed on July 28, 1995, now U.S. Patent No. 6,346,174 B1; which is a divisional of U. S. Patent Application Serial No. 08/151,229 filed on November 12, 1993, now abandoned. Still further, the study of the files of PPG shows that James J. Finley and Mehran Arbab assigned their entire rights, titles and interests in U.S. Patent Application Serial Nos. 08/151,229; 08/508,408 and 10/075,021, and to U.S. Patent No. 6,346,174 B1 to PPG, and that PPG assigned its rights, title and interests in U.S. Patent Application Serial Nos. 08/151,229; 08/508,408 and 10/075,021, and to U.S. Patent No. 6,346,174 B1 to PPG Industries Ohio, Inc, a wholly owned subsidiary of PPG.

11. The date of the stamp on the MOI and the filing date of U.S. Patent Application Serial Nos. 08/151,229 is evidence of diligence of preparation and filling a patent application covering the invention described in the MOI (Exhibit A)

12. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.


Donald C. Lepiane


Date

P MEMORANDUM OF INVENTION

Entry No. TG-93-51

To Patent Department -

AUG 18 1993

From (Location) Harmarville

Disclosed herein for consideration is a record of invention as described below:

A. BRIEF TITLE OF INVENTION

Hardened metal coatings by MSVD processing

B. PURPOSE OF INVENTION

Metal coating is hardened during sputtering for subsequent use in shipping or processing, e. g., cold end, heat strengthening, bending and tempering.

C. DESCRIPTION OF INVENTION

Oxygen gas is bled into a vacuum system along with argon gas during the sputtering of a metal. The quantity of oxygen gas is kept at levels less than that required to switch from metal to oxide sputtering mode. The coating sputtered in this range of mixed argon/oxygen gas is only slightly higher in transmission than a coating sputtered only in argon, and the sputtering rate is approximately that of the metal. The amorphous metal coating produced using this method is significantly harder than the crystalline metal coating produced by sputtering in pure argon gas. Higher oxygen/argon gas ratios produce a harder coatings. This coating could be heated to produce a haze free, dense, crystalline metal oxide coating with first surface durability. This is an extremely cost effective way to produce thick metal oxide coatings with applications as interference color coatings with selected chromas. Oxygen is the preferred gas; nitrogen has the same effect, however, the heated coating is extremely hazy. The preferred metals are titanium and zirconium. Other metals include Al, Hf, Nb and V.

Attach supplemental sheets as necessary.

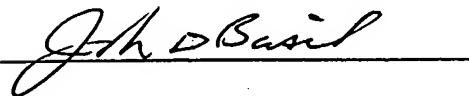
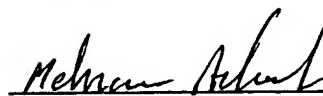
D. LIST PERTINENT PATENTS OR PUBLICATIONS KNOWN TO YOU

A. Inove, H. Vamagata & T. Masumoto; Nitrogen-Induced Amorphization in Al80Ti20 Films Prepared by Reactive Sputtering; Materials Letters 16 (1993), pages 181-184

NOTE: IN SECTIONS E, G, AND L, PLEASE TYPE OR PRINT NAMES ADJACENT ALL SIGNATURES.

E. WITNESS TO FOREGOING DESCRIPTION AND TO THE SIGNATURE(S)
OF INVENTOR(S)

SIGNATURE OF INVENTOR(S)

8/6/93
DATEAugust 6, 1993
DATEJohn D. Basil
TYPE OR PRINTJames J. Finley
TYPE OR PRINT_____
DATEAugust 6, 1993
DATE_____
TYPE OR PRINTMehran Arbab
TYPE OR PRINT

IMPORTANT: If there is any record of the invention preceding the date of this memo, please fill in the appropriate data on the reverse hereof.

F. WHEN DID THE INVENTION FIRST OCCUR TO YOU (GIVE DATE)

Sept 11,

G. WHEN AND TO WHOM, OTHER THAN THE CO-INVENTORS, DID YOU FIRST COMMUNICATE THE INVENTION (GIVE DATE)

D.S. Postupack, Sept 11,

I (WE) ACKNOWLEDGE THAT THE INVENTION WAS COMMUNICATED TO ME (US) ON THE DATE INDICATED ABOVE.

SIGNED

Dennis Postupack

TYPE OR PRINT

DENNIS. POSTUPACK

SIGNED

TYPE OR PRINT

H. WHEN AND WHERE WAS THE FIRST SKETCH, DRAWING, OR PHOTOGRAPH, IF ANY, MADE OF THE INVENTION. IDENTIFY AND ATTACH COPY.

I. WHEN WAS THE INVENTION FIRST DESCRIBED IN WRITING. GIVE DATE AND IDENTIFY NOTEBOOK, REPORT OR OTHER SOURCE. ATTACH COPY.

Sept 11, Data Book No. 6296 pages

J. IDENTIFY PERTINENT DESCRIPTIONS, REPORTS, SUMMARIES, DRAWINGS, PHOTOGRAPHS, ETS. SUBSEQUENT TO I ABOVE.

VE036 sample series deposition parameters, Wks 28 Line 8, February 5, 1993

Test results for Taber abrasion analysis of the above samples, March 22, 1993

Plant trial notes, Mehran Arbab, February 4 & 5, 1993

K. WHEN (GIVE DATE) AND WHERE WAS THE INVENTION EITHER FIRST MADE (MACHINE OR PRODUCT), OR FIRST PERFORMED (PROCESS)

Sept 11,

L. WHEN AND BY WHOM WAS THE INVENTION FIRST TESTED ANYWHERE FOR PERFORMANCE (GIVE DATE, AND NAMES OF OBSERVERS)

Sept 11, P.S. Postupack

I (WE) ACKNOWLEDGE THAT I (WE) OBSERVED THE PERFORMANCE TEST ON THE DATE INDICATED ABOVE.

SIGNED

TYPE OR PRINT

SIGNED

TYPE OR PRINT

M. HAS THE INVENTION BEEN PUBLISHED OR COMMUNICATED OUTSIDE THE COMPANY (GIVE DETAILS)

no

N. IF A PRODUCT RESULTING FROM THE INVENTION HAS BEEN USED OR SOLD ANYWHERE, STATE WHEN AND WHERE

End of year - windshields and sidelights (not oxidized) were sent to GM; Samples of oxidized coatings were shown to GM, Chrysler, Toyota

TITLE

DATE

Tues, Sept 11

Sputter Ti films under different conditions of cathode scanning speed and current for O_2 or argon flow

Ti-12 Current-15; scan-max Rate 35 7 passes to 10.5%
abrasion resistance is VG

Ti-13 Current-15 scan-max⁶ Rate 35 4 passes to 8.4%
abrasion resistance is POOR

Ti-14 Current-10; scan-max Rate 30 11 passes to 10.1%
abrasion res VG

I took pictures of Ag splot on ~~the~~ (see)
time since splot is

Wed, Sept 12

Sputter Ti films flow at 15 amps and scan of 6 with different amounts of O_2

Ti-15 Rate 36; O_2 flow 9 Ar flow 18; 8 passes
at "6" and 1 pass at "8" to 9.4% T: abrasion res
Excellent. Reflectance is brownish

~~Ref~~
Ti-16 Rate 36; O_2 flow 4.5 Ar flow 18.4; 5 passes
at "6" to 9.2% T: abrasion res - Excellent;
reflectance is slight brownish, between metallic
and Ti-15 ref.

Ti-17 Rate 36; O_2 flow 1.5; 5 passes 9.0% T abrasion excellent

Thurs, Sept 13

Sputter Ti in N_2

Ti-18 (Sputtered 9-12) Pure Argon (no O_2 or N_2)
abrasion resistance POOR

EXPERIMENT CONDUCTED BY

James J. Fink

WITNESSED BY

DATE

Sept 13

TITLE _____

DATE _____

Ti-19 Rate (17-18); N_2 flow 10.5 (Scope A-ball 55)
 12 passes to 22.4 %T; Abrasion Res - Ajax excellent
 Pinnic-poor; Bronze ref.

Ti-20 Rate 33; N_2 flow 5* (half ball); 8 passes,
 10 % T; Excellent abrasion resistance for
 both Ajax and Pinnic; Goldish reflectance
 $R = 46.2/57$

Ti-21 Rate 35; N_2 flow 1.5; 5 passes to 8.5 %T;
 Abrasion - Ajax V.G., Pinnic V.G. $R = 85.2/57$

Ti-22 Rate 27-28; N_2 flow 3.5, O_2 flow 2.5; 14 passes
 10.7 %T

Fri, Sept 14

Try glass cleaned in washer (covered)

Ti-23 Rate 35; O_2 flow - 1.5; 5 passes to 8.7 %T
 Abrasion res V.G.

McDell Try glass CeO₂ polished but no cover

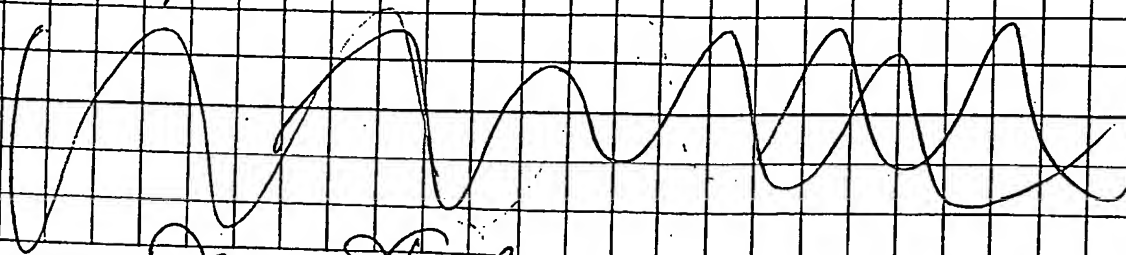
Ti-24 Rate 35; O_2 flow - 1.5; 5 passes, 7.7 %T
 Abrasion res V.G.

Look at #1503 (3rd/5th 70 - $A_3 - (I_2/S_2)O$ film
 under optical. Also no spots, defects etc.

Mon Sept 17 to Wed Sept 27

Windshields for GMI coated with Ti

Cl will give details after project
 is completed



EXPERIMENT CONDUCTED BY

James Family
 DATE Sept 27,

WITNESSED BY _____

DATE _____

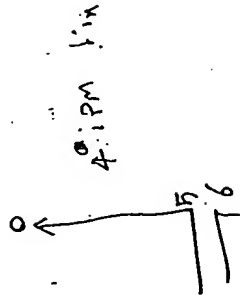
*

Also try the Zn Sn!

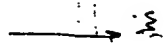
2-5-93

VE1036

35
38
41
44



5:18 PM



VE1036

Sample no	Am H ₂ O ₂ (%)	Am %	Y
VE12	38 (40)	0.022	
6	43	0.2227	0.1745 10.42
7	39	0.3139	0.2359 11.70
8	37	0.3795	0.3310 11.11
9	38	0.3545	0.2924 14.2
10	40	0.2912	0.2151 10.39
11	41	0.2655	0.1884 10.15
12 (49, 4m)	38		
13	40.5		

Creighton windshields : 12

6: at 42.4

8: at 40.5

4mm side lit

27	at 40.5 (3)	stack 33	30x 41	sample 1
9	at 48.5 (40.5)	stack 67	30x 2	sample 1
9	at 44. blue	stack 47	30x 2	sample 1
9	at 39 (7)	stack 16	30x 2	sample 1

Run ILS for 13

* 580-1 ... Cherry Blazer F.D. 8
Line 4

More than fifty 4mm side-lites (clear, 520-1 pattern) were coated with 4 Ti thicknesses targeting 4 different color coordinates. These samples were subsequently tempered on line 28-4 (W. Zimmerman). Presumably as a result of the undefined heat pattern (too few samples were available), all of the lites developed varying degrees of near-edge crazing. This issue, as well as the unknown effects of cold end processing of the coated substrate (i.e., cutting, edging, and washing) remain to be resolved.

ATD Monthly Letter

Date: 12/21/

Program Category:

Department:

Title/Project No.:

Author: MA

ATD Monthly Letter

Date: 2/22/93

Program Category:

Title/Project No.:

Department:

Authors: MA

Project Team:

Program Category:

Title/Project No.:

Department: Vacuum-Auto

Author: MA

Project Team:

* Technical Highlights: A one day trial at wks 28-8 was dedicated to a preliminary evaluation of fabrication of the monolithic, high transmission, colored coatings. This trial was based on the Pastel concept developed at the lab. (JJ Finley), where an opaque metallic Ti (or other metals or alloys) deposited on glass, is oxidized during the tempering (or bending) process. Depending on its thickness, the resulting oxide layer imparts a variety of reflective colors to the glazing. The reason for the deposition of the initial coating in the metallic mode is to exploit its high deposition rate (as compared to the reactive sputtering of, e.g., TiO_2) and to make the Pastel concept cost effective and compatible with the existing coater capabilities. The concern with this approach is, however, the mechanical durability of the metallic titanium coating.

With the help of an xy color chart generated from the laboratory samples, a specific target color (ca. $x=0.2782$, $y=0.2028$) was obtained in a short period of time. However, during this trial, we concentrated only on samples cut from the center of the coated lites; that is, the potentially significant gradient problems were not examined.

The concern about mechanical durability of the metallic coating was addressed using the partial oxidation concept similar to that used in the development of the shippable Sungate coating. The abrasion resistance of the metallic Ti coating was, thus, significantly improved upon, as indicated by a number of abrasion resistance checks.

ATD Monthly Letter

Date: 3/25/93

Program Category:

Title/Project No.:

Department:

Authors:MA

Project Team:

Program Category:

Title/Project No.:

Department: Vacuum-Auto

Author:MA

Project Team:

* Technical Highlights: A representative set of Pastel samples from last month Evansville trial was exposed to Taber abrasion tests. The tests on the pre-heat samples confirmed our initial results regarding the significant role of impurity oxygen in increasing the abrasion resistance of titanium. Also, for Taber tests exceeding 300 cycles, post-heat experiments indicated a clear dependence of the coating abrasion resistance on its thickness: in general, increasing the thickness of the coating results in a higher after-heat haze. For fully oxidized films of 21 to 28 $\mu\text{g Ti/cm}^2$, coating abrasion at 1000 cycles corresponded to a 2.4% to 3.4% range of haze; in particular, the showed a 2.9% reading after 1000 cycles. These coatings will be further tested for environmental/chemical durability.

In addition to the Pastel sidelites reported previously, windshields consisting of one Pastel color were also fabricated during the past month. The single lites were coated in Evansville and shipped to Creighton for forming. During the bending process, the coating had to be on an outer surface to be fully oxidized . For process compatibility purposes, both the shipping and forming results were very encouraging.

ATD Monthly Letter

Date: 4/26/93

Program Category:

Department:

Title/Project No.:

Author: MA

Project Team:

Objective: The monolithic Pastel coatings, consisting of thermally oxidized Ti films, were subjected to a number of chemical durability tests. Also underway are experiments aiming to determine any unique, and thus patentable, features of the process, structure, and property relationships.

Technical Highlights: 1- the pastel coatings produced previously in Evansville were tested in boiling water for up to 8 hours. Coatings that were deposited with a finite flow of oxygen in the working gas (type II coatings) remained free of defects for the duration of the test. A few isolated post-boil defects on the films deposited in pure argon (type I coating) most likely originated from mechanical damage to these softer films prior to thermal oxidation.

The "SolarCool tests" including exposure to _____ were also performed. A typical Pastel coating passed all these tests with only minor alterations after exposure to _____. According to XRF measurements, the maximum titanium loss due to any one of the above chemical tests was about 1.3%, or less. In contrast, titanium oxide films deposited by the reactive sputtering method proved to be extremely reactive and, with the possible exception of _____, failed the SolarCool Tests.

Cleveland humidity tests are in progress for both before and after heat coatings including both types I and II films. Three of the samples including both of the heated as well as the before-heat type I films, have survived the test for a minimum of _____ days without significant visual and optical alterations. The before heat type II sample has developed a rather uniform goldish reflected color associated with an increased transmission. We believe this change to be due to the

2- XRD analyses of the above coatings have revealed important structural differences between the two film types (I&II). In the case of the as-deposited films, type I samples exhibit clear diffraction patterns characteristic of β -titanium. Type II coatings, however, appear to be mostly amorphous. This difference may be due to an oxygen-induced decrease in the mobility of the adsorbed metal atoms on the surface of the growing Ti films;

As reported last month, these metastable coatings are more _____ and, according to Taber abrasion measurements, _____

If the results of the above Cleveland test can be generalized, the non-equilibrium state of type II films may also explain _____

The initial crystallinity of the Ti films has a strong effect on the structure of the heated films as well. Although all of the above films crystallize in the _____ phase, the type II films show a strong preferential _____ In addition, XRD measurements indicate that the _____

Further work is in progress in order to determine if we can _____

ATD Monthly Letter

Date: 5/21/93

Program Category:

Title/Project No.:

Department:

Author:MA

Project Team:

* Technical Highlights: A 28-day Cleveland humidity test was completed for the pre- and post-heat Pastel coatings. The heated sample with as-deposited oxygen impurity, did not develop any discernible weathering defects during the above test. The coating with no initial oxygen impurity showed some degradation, probably at sites of earlier mechanical damage (i.e., scratches) to this softer coating, emphasizing the advantageous role of O₂ in hardening the pre-heat film.

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Nitrogen-induced amorphization in $\text{Al}_{80}\text{Ti}_{20}$ films prepared by reactive sputtering

Akihisa Inoue ^a, Hiroshi Yamagata ^b and Tsuyoshi Masumoto ^a

^a Institute for Materials Research, Tohoku University, Sendai 980, Japan

^b Research and Development Division, Yoshida Kogyo K.K., Kurobe, Toyama Pref. 938, Japan

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A nitrogen-induced amorphization phenomenon was found to occur in an $\text{Al}_{80}\text{Ti}_{20}$ alloy prepared by sputtering in a flowing gas consisting of 0.98 Pa argon and 0.02 Pa nitrogen, though only an fcc phase is formed by sputtering in argon. The crystallization temperature and hardness increase from 662 to 728 K and 430 to 910, respectively, with an increase in the volume fraction of nitrogen from 2 to 7%.

It has recently been clarified [1-4] that an amorphous phase in Al-based systems is formed by rapid solidification. However, these amorphous alloys are limited to multicomponent alloy systems containing more than three components except for Al-Ln (Ln=lanthanide metal) binary alloys. There has been a strong demand for the formation of an amorphous phase in Al-based binary alloys without Ln element. We have carried out a systematic study on the formation and properties of Al-based binary amorphous alloys containing transition metal (TM) belonging to group IV to VIII as a solute element. Many trials of producing an amorphous phase in Al-TM alloys containing more than 80 at% Al were carried out by melt spinning and sputtering, but no amorphous single phase has been obtained. In the subsequent study on the formation of an amorphous phase in Al-based alloys, it was found that the dissolution of a small amount of nitrogen is very effective for the formulation of an amorphous phase in Al-rich composition ranges. This paper is intended to present the formation of amorphous films in $\text{Al}_{80}\text{Ti}_{20}$ by sputtering in an argon gas atmosphere containing a small amount of nitrogen, and their thermal stability and mechanical properties and to investigate the effect of the nitrogen-induced amorphization on their properties.

An $\text{Al}_{80}\text{Ti}_{20}$ (at%) alloy target with a disk shape of 75 mm in diameter and 6 mm in thickness was

prepared from pure Al with a purity of 99.99 mass% and pure Ti with a purity of 99.9 mass% by arc melting in a purified argon atmosphere. The premelted target was sputtered on a glass substrate to form a film with a surface shape of $50 \times 50 \text{ mm}^2$ and a thickness of about 1.3 mm using a dc magnetron sputtering apparatus. After evacuating the sputtering chamber mounted with the target material up to 6×10^{-5} Pa, an argon gas or mixed argon and nitrogen gases of 1.0 Pa were fed through an automatic gas-flow controller to make argon plasma in the chamber. The partial pressure of nitrogen to argon plus nitrogen (P_N) was changed so as to be 0, 0.02, 0.04, 0.06, 0.07, 0.09 and 0.1 Pa. The argon plasma was generated between the substrate cathode and stainless-steel anode. The supplied anode current was usually 300 mA and the anode voltage was 0.45 kV. The sputtering time was adjusted to be 7.2 ks. Prior to sputtering target, the substrate was sputtered to clean its surface for 600 s by applying a negative bias against the substrate. The gap between the target and substrate was fixed at 60 mm. The analysis of the nitrogen element in the sputtered films was made by electron-probe microanalysis.

The as-prepared structures for the sputtered films were examined by thin-film type X-ray diffractometry using Cu K α radiation and transmission electron microscopy (TEM). The 2θ angle in the X-ray diffractometry was calibrated with Si powder. The

thin foils for TEM were prepared by cutting the sputtered film with a microtome. The crystallization temperature was measured at a heating rate of 0.33 K/s with a differential scanning calorimeter. Measurements of electrical conductivity were made at room temperature (≈ 290 K) by a conventional four-probe technique. Knoop hardness was examined by using a Vickers microhardness tester with a Knoop indenter and a load of 10 g.

Fig. 1 shows the change with P_N in the X-ray diffraction patterns of the sputtered $Al_{80}Ti_{20}$ films. The incident angle of the X-ray beam to the specimen surface was fixed to be 2.5° . Although the as-sputtered structure consists of an fcc phase at $P_N=0$ Pa, the increase of P_N to 0.02 Pa causes the structural change from an fcc to an amorphous phase. The formation of the amorphous phase is kept in the P_N range below 0.07 Pa and the further increase in P_N results in the formation of a mixed structure consisting of amorphous and hexagonal AlN. It is thus to be noticed that the mixing of a small amount of nitrogen in the sputtering atmosphere is very effective for the formation of an amorphous phase, indicating the achievement of nitrogen-induced amor-

phization in the Al-based alloy. Furthermore, it is seen in fig. 1 that the peak position in the broad diffraction peak revealing the formation of an amorphous phase shifts continuously to a lower-angle side with increasing P_N . Fig. 2 shows the change in the wave vector (K_p) at the peak position with P_N . K_p decreases almost linearly from 51.40 to 49.84 nm^{-1} in the P_N range 0.02–0.07 Pa and then more steeply in the higher P_N range. The linear decrease in K_p with P_N is thought to originate from the dissolution of nitrogen into the films. Also, the increase in the degree of the decrease in K_p around $P_N \approx 0.08$ Pa is presumably due to the structural change from an amorphous to an amorphous plus AlN phase.

In order to confirm the formation of the amorphous phase by the dissolution of nitrogen, TEM observations were carried out for the sputtered films prepared at $P_N=0$ and 0.02 Pa. Fig. 3 shows bright- and dark-field electron micrographs and a selected-area diffraction pattern of the $Al_{80}Ti_{20}$ film prepared at $P_N=0$ Pa. The diffraction rings shown in fig. 3b can be identified to be an fcc structure and the dark-field micrograph taken from the (111) reflection ring reveals that the fcc phase consists of very fine grains with a mean size of about 40 nm. Thus, no trace indicating the formation of an amorphous phase is seen in fig. 3. Fig. 4 shows a bright-field electron micro-

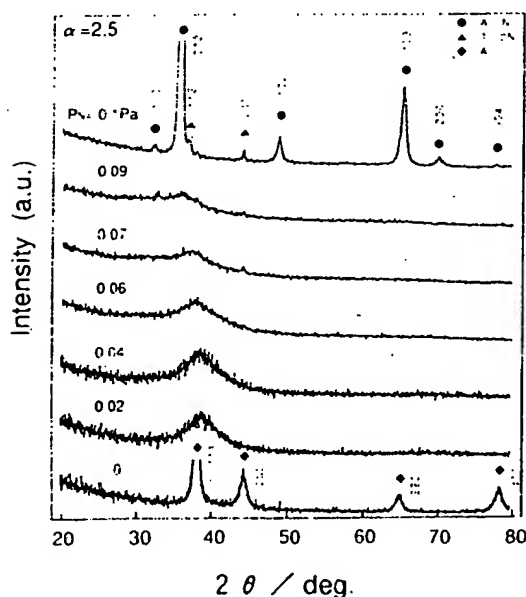


Fig. 1. X-ray diffraction patterns of the films prepared by sputtering an $Al_{80}Ti_{20}$ alloy in the atmospheres in which the P_N was changed to be 0, 0.02, 0.04, 0.06, 0.07, 0.09 and 0.1 Pa.

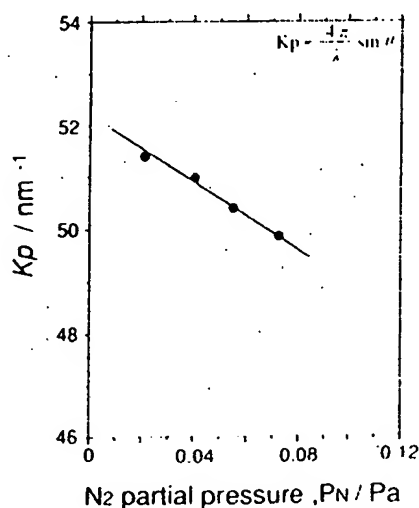


Fig. 2. Wave vector ($K_p = 4\pi / \lambda \sin \theta$) of the peak position of an amorphous halo in the X-ray diffraction patterns shown in fig. 1 as a function of P_N .

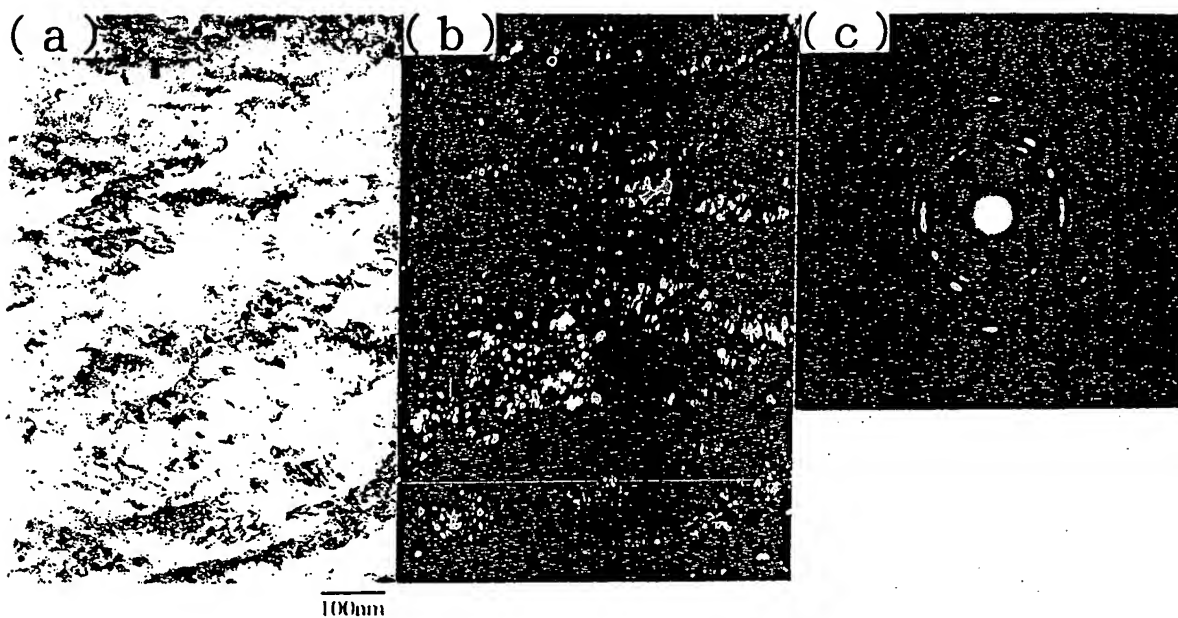


Fig. 3. Bright-field (a) and dark-field (b) electron micrographs and selected-area diffraction pattern (c) of an $\text{Al}_{60}\text{Ti}_{20}$ film prepared by sputtering at $P_N = 0$ Pa.

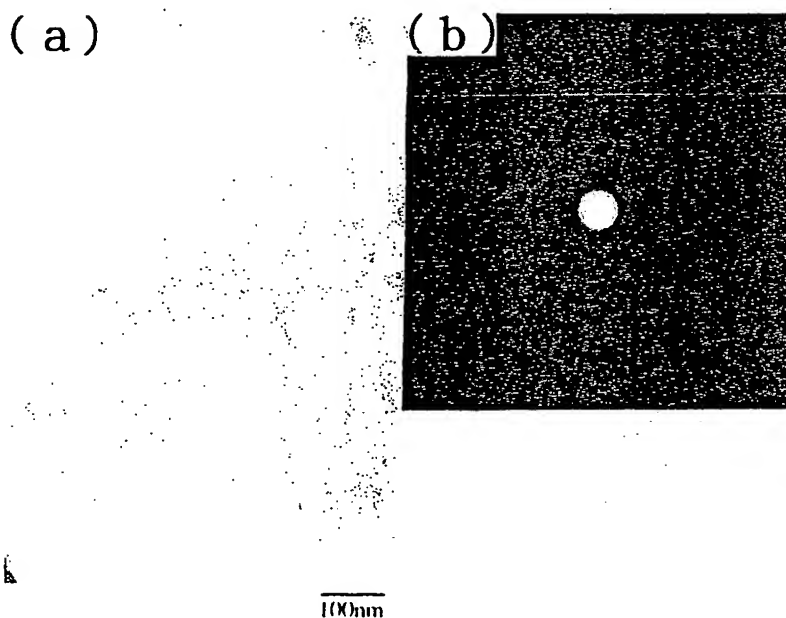


Fig. 4. Bright-field electron micrographs (a) and selected-area diffraction pattern (b) of an $\text{Al}_{60}\text{Ti}_{20}$ film prepared by sputtering at $P_N = 0.02$ Pa.

graph and a selected-area diffraction pattern of the sputtered $\text{Al}_{80}\text{Ti}_{20}$ film prepared at $P_N = 0.02$ Pa. No contrast revealing the existence of a crystalline phase is seen in the bright-field image and the diffraction pattern consists only of broad rings. The results shown in figs. 3 and 4 indicate clearly that the dissolution of nitrogen is very effective for the increase in the glass-forming ability for the Al-based alloys. This phenomenon can be regarded as nitrogen-induced amorphization.

It is expected that thermal stability and mechanical strength of the amorphous films change significantly with nitrogen content. Fig. 5 shows the changes with P_N in the onset temperature of crystallization (T_x) and the Knoop hardness number (H_k) of the sputtered amorphous $\text{Al}_{80}\text{Ti}_{20}$ films. As P_N increases from 0.02 to 0.07 Pa, T_x and H_k increase almost linearly from 662 to 728 K and from 51.40 to 49.84 nm^{-1} , respectively. This result indi-

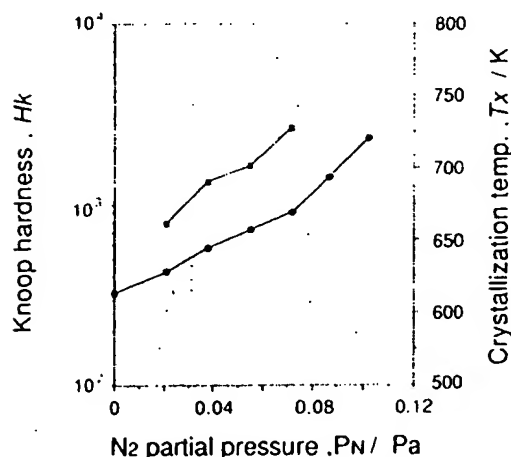


Fig. 5. Crystallization temperature (T_x) and Knoop hardness number (H_k) as a function of P_N for the amorphous $\text{Al}_{80}\text{Ti}_{20}$ films prepared by sputtering.

cates clearly that the dissolution of nitrogen is very effective for the increase in thermal stability and mechanical strength, in addition to the increase in the glass-forming ability. Furthermore, one can notice a close correlation between T_x or H_k and K_p from the data shown in figs. 2 and 5. It is therefore concluded that the changes in T_x and H_k for the amorphous films are dominated by the nitrogen content in the amorphous phase.

In conclusion, it was found that mixing of 2 vol% nitrogen to an argon sputtering atmosphere caused the formation of an amorphous single phase in an $\text{Al}_{80}\text{Ti}_{20}$ alloy, though only an fcc solid solution was formed in the film prepared by sputtering in an argon atmosphere. T_x and H_k increased from 662 to 728 K and from 430 to 910 with an increase in the partial pressure of nitrogen from 0.02 to 0.07 Pa. It is therefore concluded that the dissolution of nitrogen into the Al-based alloy is effective for the increase in the thermal stability and mechanical strength as well as for the increase in the glass-forming ability. The utilization of this concept is expected to bring about new amorphous Al-based alloys with better engineering properties in higher Al-concentration ranges.

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EXHIBIT B

PPG INDUSTRIES, INC.

INTER-OFFICE CORRESPONDENCE

	DATE:	August 23, 1993
	FROM:	D. L. Seidel
TO: J. J. Finley M. Arbab	LOCATION:	Patent Department, 39 West
	SUBJECT:	TG-93-51 Category--Cathode Sputtered Coatings

This will acknowledge receipt of your disclosure dated August 6, 1993, and entitled "HARDENED METAL COATINGS BY MSVD PROCESSING."

Patent Department No. TG-93-51 has been assigned to this disclosure.

D. L. Seidel
D. L. Seidel
Assistant Patent Counsel
Glass

DLS/dmk

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